# ENVIRONMENTAL EFFECTS OF SPECIAL WASTE

for

Ontario Waste Management Corporation

by

**ELI Eco Logic Incorporated**
Acton, Ontario, Canada

March 28, 1987.

90-02958/

March 29, 1987.

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Dear Dr. Mitchell.

We are pleased to present our final report on Environmental Effects of Special Waste. The report includes two appendices: Appendix A: Great Lakes Areas of Concern, and Appendix B: Exposure and Toxicity Profiles of Chemicals Found in the Great Lakes. We feel that this report strongly supports an urgent need for better management of special waste in Ontario.

Yours very truly,

Douglas Hallett

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President

DJH/mh

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# EXECUTIVE SUMMARY

## Purpose of the Report

The Ontario Waste Management Corporation is engaged in developing a waste management option for Ontario. At the outset it is necessary to ascertain the current impacts on human health and the environment due to toxic chemicals derived from special industrial waste in Ontario. These impacts must consider:

a) what are the key chemicals,

b) where do they occur,

c) what are their spatial and temporal trends in Ontario,

d) what are the key species and populations currently being affected,

e) what effects are observable,

f) what other potential effects might be occurring, and the seriousness of these effects.

## Scope and Method

This analysis first considers the occurrence of toxic chemicals in the Ontario environment which come from special waste (Chapter 2). **Special waste is defined by OWMC as liquid industrial and hazardous waste that cannot be handled effectively by conventional municipal treatment and disposal facilities such as sanitary land-fills, municipal incinerators and sewage treatment plants.** The spatial trends of chemicals on a national, provincial, regional and local basis are examined from the published literature and government reports. The most common chemicals which originate from special waste (vs. agricultural application of pesticides or naturally occurring compounds) and which bioaccumulate in the food chain or bioconcentrate and persist in living organisms including human tissues are selected for intensive review. Temporal trends in monitoring data are considered to determine immediate problems shown by rising trends, continuing problems shown by stationary trends and lesser problems which now have rapidly declining trends.

Exposure and observable effects on environmental species are then considered at the regional and local levels (Chapter 3). Cause-effect relationships are established where possible on wild species. Species considered include: resident and migratory colonial-nesting fish-eating birds such as herring gulls, cormorants and terns; fish-eating mammals such as mink and Beluga whales; and fish.

Exposure pathways are analysed including the human food chain (Chapter 4). This analysis is then used to point to the major priority environmental sources of special waste and to their locations.

The reasons for these sources are explored including: the impact of current waste disposal practices; data on major municipal and industrial sources; technological problems; current regulation enforcement practices; and regulatory change (Chapter 5).

The analysis is verified by third party opinion (Chapter 6) from other more broadly based reviews such as the recent Great Lakes Water Quality Agreement Review by the US National Research Council and Royal Society of Canada and the report of the Niagara River Toxic Chemicals Committee.

## Premises and Postulates

This analysis is not based on any preferred management option selected by OWMC. The major postulate is that the toxic chemicals for which widespread exposure and detrimental effects have been demonstrated are the priority chemicals to be reduced environmentally. The sources of these chemicals are the priorities to be mitigated by the hazardous waste management options considered. Chemicals derived in part from long-range atmospheric transport and other routes outside of Ontario as well as the effect of irretrievable in-situ sources such as contaminated sediments are also considered.

## Limitation of The Data

This analysis relies on a review of the published scientific literature, government reports and available data. However this is the only material that is useful for establishing the need for management of special waste on a scientific basis.

# Major Findings

1. Current Trends of Toxic Chemicals in the Ontario Environment (Chapter 2).

a) Of the major environmental contaminants which are found in the Ontario environment the majority are derived from persistent industrial chemicals found in special waste, and as combustion products in municipal incinerators with the rest resulting from the application, primarily in the past, of hard pesticides such as DDT which biodegrade very slowly (see section 2.5).

b) The contaminants which are found are present because of their environmental persistence, their ability to bioaccumulate, and the prevalence of their sources.

c) The Ontario ecosystem, is particularly susceptible to persistent toxic chemicals because of the retention time of the Great Lakes, and the propensity of these compounds to cycle between the large bodies of water and the atmosphere. In addition, these lakes are now particularly sensitive because large in-situ areas of contaminants, which have built up over the past 40 years, which act as continuous sources to the water column.

d) The atmosphere has become the major pathway of transport for persistent toxic chemicals to Ontario land and water.

e) Localized and widespread trends of environmental contaminant levels show rapid declines during the period from

1970 to 1980 which are likely due to the initial legislation which restricted the chemical manufacture or usage of certain compounds such as DDT or PCBs; the better industrial treatment of aquatic effluents; and the reduction of gross toxic chemical pollution which was evident in the Niagara River about 1960.

f) Since 1980, although many localized trends of environmental contaminants continue to show a decline, widespread trends such as whole lake trends of certain environmental contaminants in Lake Ontario have become stationary while others show an increase. In other areas such as Lake Superior marginally slow declines continue.

g) The increases and slowly declining trends are evidence of continuing environmental sources of persistent chemicals derived from special waste. These chemicals are entering the Ontario ecosystem at a rate which varies above for increasing trends and below for decreasing trends the rate by which they are being effectively removed from circulation. Exposure of biota including humans is caused by the continuing circulation of the contaminants within the ecosystem.

2. Impact of the Major Toxic Chemicals Originating from Special Waste in Ontario (Chapter 3).

a) Population level effects, such as reproductive failure, increased incidence of congenital anomalies and abnormal behaviour in wild omnivorous or carnivorous birds of Ontario, reproductive failures of mammals such as mink, and increased incidence of fish tumours have been scientifically documented since the 1960s.

b) Although the widespread gross population effects such as the almost total reproductive failure of herring gulls, cormorants and herons in Lake Ontario stopped in 1977, other more subtle effects such as liver enzyme disfunction, and elevated incidence of fish tumours still occur in localized areas of the Great Lakes. Ontario mink cannot be fed Great Lakes fish as a source of protein, and herring gulls from certain areas such as eastern Lake Superior still exhibit reproductive failures.

c) Cause-effect relationships at the population level are evident for polynuclear aromatic hydrocarbons and certain fish tumour problems, and between chlorinated hydrocarbons such as PCBs, chlorobenzenes, chlorinated dioxins, and dibenzofurans and certain chlorinated pesticide residues and the reproductive problems found in Great Lakes herring gulls.

d) The Beluga whale population in the St. Lawrence River is currently suffering from reproductive impairment probably caused by the same toxic chemicals found in Lake Ontario.

e) Population-level effects in wild species represent serious problems from toxic chemical exposure since documented cause-effect relationships show long lag phases of more than 10 years duration between the chemical exposure and the population damage and between the decline of exposure and the improvement within the population. Therefore population-level effects in wild species (caused by toxic chemicals) represent serious problems since the effect may last for over 10 years after the cause has been removed.

f) The effects demonstrated in wild Ontario populations represent irreversible or terminal damage to the individuals within each species studied. These effects, such as total reproductive failure, would be considered totally unacceptable if they were demonstrated in human populations in Ontario especially if cause-effect relationships could be established.

3. Ecosystem Pathways and Human Exposure Routes to Special Waste (Chapter 4).

a) Ontario citizens are exposed to and are bioaccumulating the same residues derived from special waste as those present in wild populations.

b) Levels of chlorinated dioxins in human body fat sampled to date are equivalent to those found in Lake Ontario alewives and smelt and are within a factor of 10 to 100 of those found in populations of fish and birds experiencing population-wide effects.

c) The main exposure route to humans in Ontario of these residues from special waste such as PCBs or chlorinated dioxins is via food grown in Southern Ontario.

d) The food derived from the Ontario terrestrial ecosystem (cropland) is contaminated via the atmosphere in the same fashion as the fisheries resource derived from the Great Lakes aquatic ecosystem is contaminated via the atmosphere.

e) Exposure routes such as drinking water supplies in major Ontario cities represent such a minor route of exposure that mitigation of human exposure through treatment of drinking water would not significantly reduce the current human exposure to toxic chemicals derived from special waste.

f) The elevated exposure rate or dosage of certain human sub-populations such as newborns, children or occupationally exposed groups is more critical.

g) Removal of the sources of special waste which stem from improper disposal and treatment appears to be the only practical and effective solution.

4. Sources of Priority Chemicals (Chapter 5).

a) The two general sources of residues derived from special waste entering the Ontario environment are industrial discharges from many sectors and municipal treatment plants which are contaminated with industrial waste.

b) Current incineration practices, particularly for sewage sludge and municipal refuse contaminated with industrial residues add to the contamination problem caused by either the dispersion of the industrial residues through the atmosphere, or via the creation of more highly toxic byproducts such as chlorobenzenes, chlorinated dioxins and chlorinated dibenzofurans.

c) Alternately, if the industrial special waste entering municipal treatment systems were removed and treated at the source by best available technology the emissions and discharges mentioned above in both a and b would be greatly reduced.

d) The primary persistent organic contaminants coming from Ontario industrial discharges, particularly in the St. Clair River area and international discharges in the Niagara River area, are found as contaminants in Ontario wildlife, fish, humans and food. These residues include PCBs, chlorobenzenes, chlorostyrenes, chlorinated dioxins and dibenzofurans, chlorophenols, and polynuclear aromatic hydrocarbons.

e) Industrial spills and accidental discharges are currently a major source of special waste to the environment which could be controlled by better waste management. Chemicals and special waste which have been recovered from spills also require better means of treatment so that they will not become a future problem.

f) Leachate from old landfills and seepage from deepwell disposal practices are also environmental sources of residues derived from special waste in Ontario. Problems are evident on the St. Clair River and Niagara River. Ontario has classified 69 active waste sites, and 99 closed waste sites that have received industrial liquid or hazardous waste as a concern due to potential impact on human health (MOE, 1986). Their contents or at minimum the leachate collected from these facilities may well be considered a significant source of special waste to the Ontario environment.

g) Ontario data on sources of special waste in the environment are very limited particularly for organic contaminants. Major loadings of persistent contaminants requiring better management are documented as coming from iron and steel mills, pulp and paper mills, refineries, petrochemical industries, and municipal treatment plants.

5. Review of Major Environmental and Policy Documents Relating to Special Waste Problems (Chapter 6)

a) The major findings found in chapters 1 to 5 are consistent with and supported by those of the International Joint Commission Great Lakes Water Quality Board, the International Joint Commission Human Health Effects Committee, the joint review of Great Lakes Water Quality by the U.S. National Academy of Science and the Royal Society of Canada, and of the World Conference on Large Lakes.

b) The chemicals of concern in all cases are consistent and emphasize persistent organic compounds such as PCBs, chlorobenzenes, chlorophenols, chlorinated dioxins and dibenzofurans and some persistent pesticides.

c) The sources to be remediated are consistent and chemicals derived from special waste are emphasized in municipal and industrial discharges as well as incineration, emissions, landfills, and contaminated sediments.

d) All of these documents emphasize the need for better treatment of special waste, a preventative approach, and better public information.

## Conclusions and Recommendations

1. The major findings of this study support an urgent need to reduce environmental exposure to persistent toxic chemicals derived from special waste from Ontario sources.

2. Environmental exposure to persistent toxic chemicals derived from special waste is currently damaging the health of wild populations in Ontario. Since human exposure has been demonstrated to be only slightly lower than affected wild populations the potential for damage to human health is great.

3. Environmental exposure to persistent toxic chemicals derived from special waste can only be mitigated practically and effectively by stopping emissions and discharges at the source of the waste and through the implementation of management practices which destroy all persistent toxic organic residues in the waste and immobilize those inorganic residues which cannot be destroyed.

4. The major postulate of this report was that the toxic chemicals for which widespread exposure and detrimental effects have been demonstrated are the priority chemicals to be reduced environmentally. The chemicals which fit this priority are chemicals that persist and for which considerable historical

pollution has already occurred. Many of these chemicals are derived from special waste and it is obvious that the current sources are not adequately addressed by enforceable legislation. Most of these sources can be removed by better waste management. This requires proper destruction technology rather than storage for organic waste, and neutralization and immobilization pretreatment prior to landfilling for inorganic wastes. The use of on-site and off-site treatment facilities will be necessary.

5. Environmentally persistent chemicals which are relatively well documented such as PCBs and chlorinated dioxins are not the only chemicals derived from special waste that may be a problem. Approximately 565 chemicals were proven to be present in the Great Lakes after thorough scientific scrutiny of a 1983 inventory. Adequate toxicology and exposure data are not available to determine scientifically whether they pose a problem. Theoretical information on these chemicals is currently being sorted out by scientists in the U.S.A. and Canada in order to decide which chemicals warrant the expense and time required for further study.

The chemicals identified in this study were either derived from pesticide application, combustion, or from industrial production. The majority of chemical types found are industrial organic chemicals. Far more chemicals likely exist in the Ontario environment and many have been reported in the scientific literature since 1983.

One general rule holds for all Great Lakes sources of chemicals derived from special waste so far. Proper treatment of either the organic or inorganic chemicals found in special waste will remove chemicals of both known and unknown toxicity.

This report therefore concludes with the message that was clearly emphasized in 1985 by the joint National Academy of Science / Royal Society of Canada Report and by all four panels convened at the 1986 World Large Lakes Conference: the most logical scientifically based course of action is to prevent and anticipate toxic chemical problems before they are proven to be occurring. For the special waste that society must create this requires treatment and disposal using best available technology.

# CHAPTER 1

# INTRODUCTION

The concern for toxic chemicals in the environment arose with the discovery of DDT in the 1950s and PCBs and mercury in the 1960s. All three of these compounds were shown to be persistent in the environment, to have bioaccumulated up aquatic food chains, from low unmeasurable concentrations in water, into plankton and zooplankton, and finally into fish, fish-eating birds, mammals, and in isolated cases, humans. Terrestrial food chains were also important since populations of avian raptors or falcons and eagles were placed in jeopardy by the eggshell thinning phenomenon caused by the accumulation of high levels of DDT. Colonial-nesting fish-eating birds such as cormorants, terns, and herring gulls were also placed in jeopardy in the Great Lakes area due in part to eggshell thinning caused by DDT. Unfortunately as studies on DDT continued, other industrial contaminants such as PCBs were discovered in the same species of wildlife. Other effects on reproduction, particularly direct embryotoxicity in eggs became evident. Methyl mercury was discovered in loons residing on Lake St. Clair during the 1960s. These loons were also experiencing reproductive failures.

These three contaminant problems occurred due to minute quantities of the individual waterborne contaminants which were virtually invisible relative to classically measured forms of pollution such as BOD (biological oxygen demand), E. coli (bacteria) and phosphates which had been entering the ecosystem continuously over a considerable period of time. The latter forms of pollution resulted in visible problems such as fouled beaches, fish kills, and odour problems. The three chemicals had also bioaccumulated up aquatic food chains because of their stability or persistence in the environment, their resistance to rapid metabolism, and their lipophilicity (fat-loving nature). This bioaccumulation and bioconcentration within the food chain caused severe reproductive anomalies which jeopardized the populations affected.

Since 1970, knowledge of the toxic chemical problem has expanded at an exponential rate because of advances in analytical chemistry allowing for the detection of trace quantities of over 1000 substances present in the Great Lakes by 1983, and from advances in modern toxicology allowing for the rapid testing and molecular understanding of the diseases caused by toxic chemical exposure.

Within the Great Lakes basin one cannot manage 1000 individual chemical problems. However it is possible to analyse the 15 to 20 general chemical classes relating to specific source types which require better management. Other than pesticides all of the source types of toxic chemicals found in the Great Lakes basin can be related to the past and present disposal of industrial special waste and municipal solid waste. Better mangement of special industrial waste relates not only to the removal of key chemical classes from aquatic effluents and atmosphere emissions but also to the permanent disposal of special waste residues which cannot be recycled once they are removed from effluents.

The major focus of this document is to evaluate the need to reduce or eliminate the widespread occurrence of persistent toxic chemicals found in the environment today. These chemicals, because of their propensity to bioaccumulate and to cause multiple chronic effects, have caused population failures in wild species in the past and are causing stress to populations of wildlife and humans throughout Ontario in the present.

# CHAPTER 2
# CURRENT TRENDS OF TOXIC CHEMICALS IN THE ONTARIO ENVIRONMENT

## 2.1 ECOSYSTEM PATHWAYS IN THE GREAT LAKES

The Great Lakes ecosystem is extremely sensitive as well as being relatively polluted with persistent toxic substances. The high surface to volume ratio allows the lakes to capture large quantities of persistent substances from dry and wet deposition of contaminants arriving via long range atmospheric transport. The long residence time of the lakes causes these chemicals to build up. This phenomenon has been exemplified with chemicals such as polychlorinated dibenzofurans and dioxins, which along with PCBs, and toxaphene are found in the sediments and fish of Lake Siskiwit, a remote lake found on Isle Royale, in north central Lake Superior. This island has neither industry, agriculture, nor logging (Czuczwa and Hites, 1986, Swain, 1982). The deposition rate of chlorinated dioxins and dibenzofurans on this island matches the deposition rate in Lake Superior. The common source of these contaminants for both of these lakes is the atmosphere. In addition up to 85 % of the PCBs and 100 % of the toxaphene enters Lake Superior from the atmosphere (Eisenreich et al., 1981).

Atmospheric transport of persistent toxic organic substances is the major pathway within ecosystems. Although the atmosphere is the major pathway, the major sources to the atmosphere are the problems. For dioxin, volatilization of residues from contaminated soils into the atmosphere was first noted as a concern at Seveso, Italy (Hallett and Hutter, 1982). In 1982 the National Research Council of Canada reported that atmospheric emissions from low temperature incinerators were the major source of chlorinated dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs) in the Canadian environment (NRC, 1981). Many incinerators also emit PCBs, chloro-phenols, and chlorobenzenes as well as many metallic contaminants (MOE, 1985a). The Ontario Ministry of the Environment estimates that 8 to 10 kg/a of 2,3,7,8, TCDD equivalents (the most toxic isomer of the PCDD, PCDF classes) enter the Ontario environment from combustion of municipal refuse and sewage sludge (MOE, 1985a). Both municipal refuse and sewage sludge currently contain many industrial or special wastes such as PCBs, chlorobenzenes and heavy metals. These contribute to emission of these compounds as well as to the formation of PCDD and PCDF emissions from low temperature incinerators currently in use for the reduction of municipal solid waste and sewage sludge in Ontario. All other combustion sources from Ontario contribute from 20 - 50 kg/a 2,3,7,8 - TCDD equivalents (MOE, 1985a). The only other major source of chlorinated dioxins and dibenzofurans stems from the use and disposal of chlorinated phenols.

## 2.2 LOCAL TRENDS

### 2.2.1 INTRODUCTION

Local trends of toxic chemicals within the Great Lakes basin demonstrate the spatial distribution of major sources of persistent toxic chemicals in Ontario as well as loadings coming from these sources. The sediment record provides an historical map of pollution of this type. This section is intended to not only describe the Ontario situation but also to differentiate between the localized declining trends of toxic chemicals caused by aquatic effluent reductions, and the more widespread trends of the same chemicals showing a stationary pattern because of other environmental sources.

### 2.2.2 SEDIMENTS

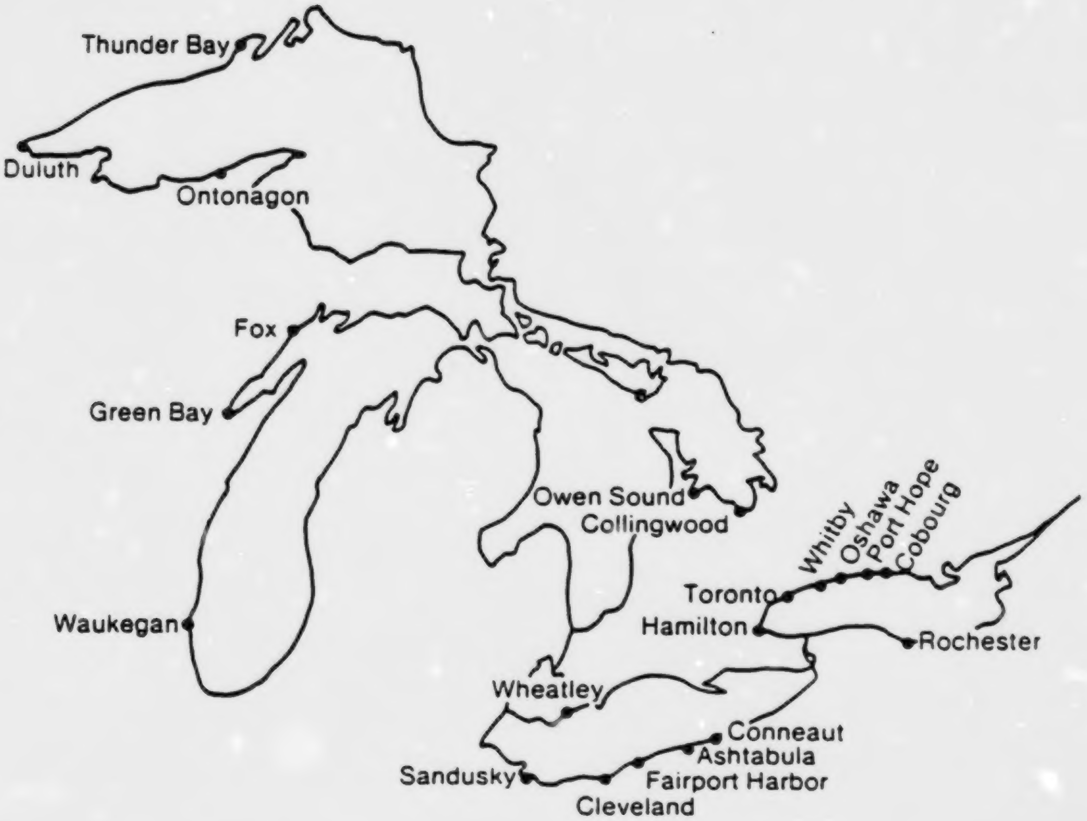
In the Great Lakes some dramatic trends in persistent residues have been observed, particularly in Lake Ontario. Spatial trends in sediment have indicated that industrial centres on the lower Great Lakes ie. Lake Erie and Lake Ontario have contributed vast quantities of mercury, PCBs, and lead to the water.

The sediment record on the Great Lakes clearly shows that the most severe contamination from toxic chemicals of industrial origin occurs either downstream of the major connecting channels, or in those harbours and tributaries which are surrounded by dense populations and heavy industry. The latter includes Toronto Harbour, Hamilton Harbour, the Bay of Quinte and Thunder Bay Harbour. Sections of the St. Mary's River, the St. Clair River, the Detroit River and the Niagara River comprise the former. The toxic chemicals most prevalent in each area are the chemicals associated with the industries adjacent to those water bodies (IJC, 1978). PCBs and chlorinated dioxins are excellent examples of special waste to follow since the best current scientific data bases are available for these compounds.

PCBs have been measured in sediments of the Great Lakes (Glooschenko et al., 1976; Veith et al., 1977; Eisenreich et al., 1979; Thomas and Frank, 1982) and extensive surveys have been conducted in Lakes Erie and St. Clair (Frank et al., 1977), Lake Ontario (Frank et al., 1979), Lake Huron (Frank et al., 1979), Bay of Quinte (Frank et al., 1980), Lake Michigan (Frank et al., 1981), and Lake Superior (Frank et al., 1982). Great Lakes harbours with PCB concentrations > 50 ug/L (Ontario Ministry of the Environment guideline for open water disposal) are shown in Figure 1 (Thomas and Frank, 1982; IJC, 1982). These harbour sediments must therefore be regarded as special waste requiring a means of proper disposal. Contaminated harbours appear to be concentrated in the lower highly industrialized Great Lakes. Heavily contaminated lake, river, and harbour sediments will

Figure 1

Great Lakes Harbours with
PCB Concentrations > 50 ug/L


Thunder Bay
Duluth
Ontonagon
Fox
Green Bay
Waukegan
Owen Sound
Collingwood
Whitby
Oshawa
Port Hope
Cobourg
Toronto
Hamilton
Rochester
Wheatley
Conneaut
Ashtabula
Sandusky
Fairport Harbor
Cleveland

Source: Thomas and Frank, 1982.

remain as continuing localized sources of PCBs due to sediment resuspension as long as they are present.

### 2.2.3 URBAN DUST

Urban dust or the local fallout in major cities is characteristic of the local sources of toxic chemicals produced there. Distinct pattern changes for polychlorinated dioxins and dibenzofurans (PCDDs and PCDFs) are evident in urban dust from various cities (Czuczwa and Hites, 1986).

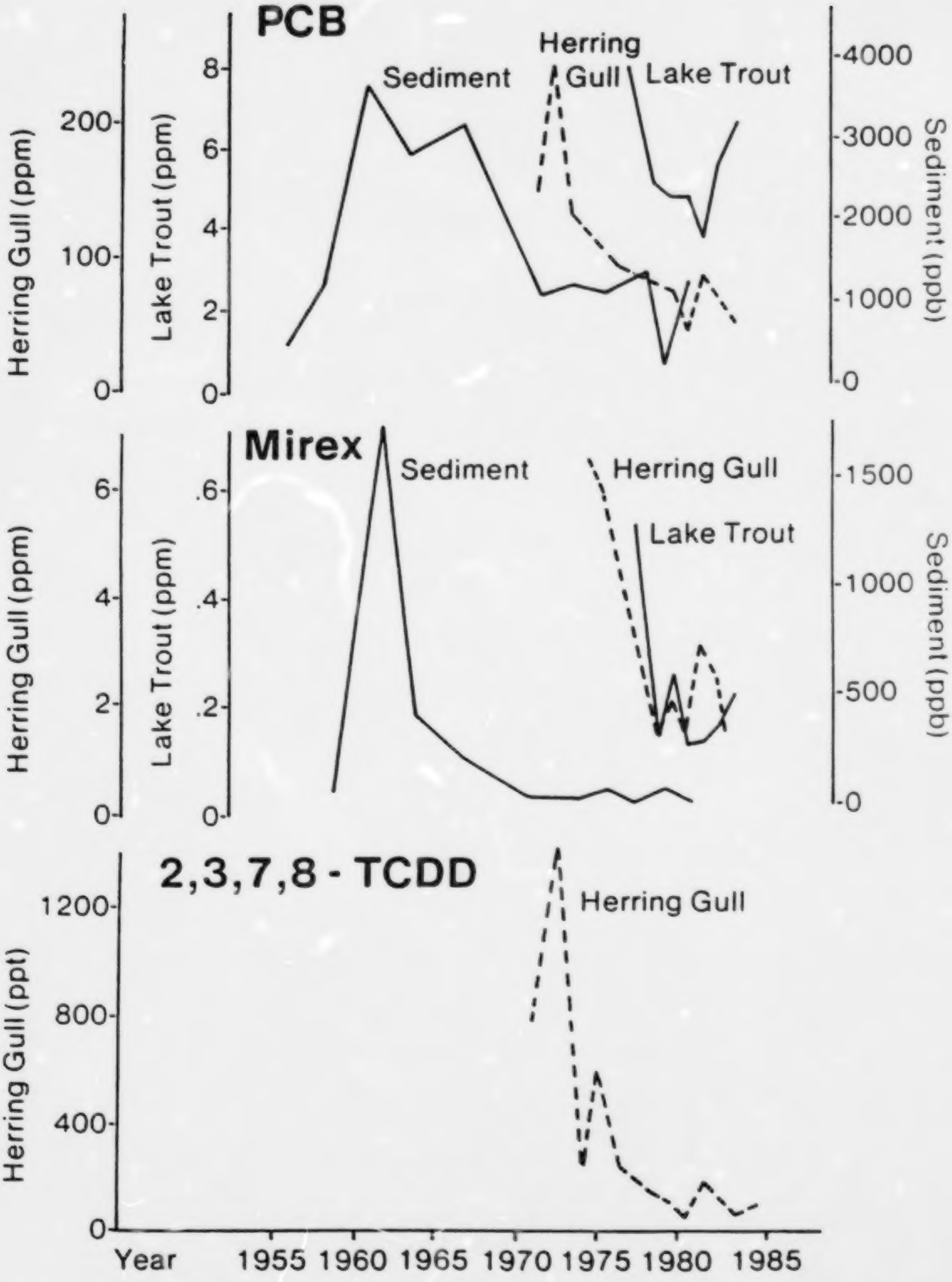
This is not surprising considering the major combustion sources of dioxins in urban centres. The predominant combustion sources in the city of Toronto on Lake Ontario, ie. the Commissioner Street municipal waste incinerator and the Ashbridges Bay sewage sludge incinerator, are different from the SWARU incinerator in Hamilton (MOE, 1985). These differences are due to the variation in the feedstock as well as the operating conditions of the incinerators in the different cities. Feedstock differences relate to the quantities of waste chemicals such as PCBs, chlorophenols, and chlorobenzenes found in the sewage sludge and solid waste. The actual toxicity as measured by the 2,3,7,8, TCDD equivalents varies considerably from one source to another. Limited samples of soils near industrial incinerators at Midland Michigan show elevated levels of PCDDs ranging from ng/g to ug/g whereas rural areas show non detectable levels. Urban areas near municipal incinerators in Chicago show detectable levels of PCDD but at levels ranging from pg/g to ng/g (Dow Chemical Co., 1978). Similar results were found in Hamilton, Ontario near a municipal waste incinerator (MOE, 1984b).

### 2.2.4 THE NIAGARA RIVER

The Niagara River area represents one of the most closely studied areas of high toxic chemical contamination. Temporal trends show a confusing situation. On first glance one can see a dramatic improvement in Lake Ontario residues of PCBs, mirex and dioxin particularly in wildlife and fish between 1970 and 1980 (Figure 2). However from 1980 to 1984 the downward trend stopped for all of these residues. The sediment record at the source of Lake Ontario shows a deposition rate for PCBs and mirex from 1950 to 1960 at approximately the present day rate. However at about 1960 a tremendous pulse of PCBs, mirex, chlorobenzenes, and hexachlorobutadiene is shown in the sediment record and the deposition rate tapers off to 1970 when it plateaus at about the 1950s rate (Durham and Oliver, 1983). Figure 2. The Niagara River still contains PCBs, mirex, chlorinated dioxins and dibenzo-furans. The current sources are most likely leachate from the series of landfills in the area containing over 200 million tonnes of chlorinated waste (Hallett and Brooksbank, 1986). The serious pollution evident in 1960 likely represents

**Figure 2**

Contaminated trends in
the Lake Ontario ecosystem.



**Source: Durham and Oliver, 1983.**

more direct sources of waste and a period of high organochlorine chemical production and use of PCBs in open industrial systems. The phenomenon of rapid declines near industrial areas during the late 1970s is quite common in the Great Lakes basin and likely reflects either better control of effluents or lower production of the key persistent contaminants.

### 2.2.5 SAGINAW BAY

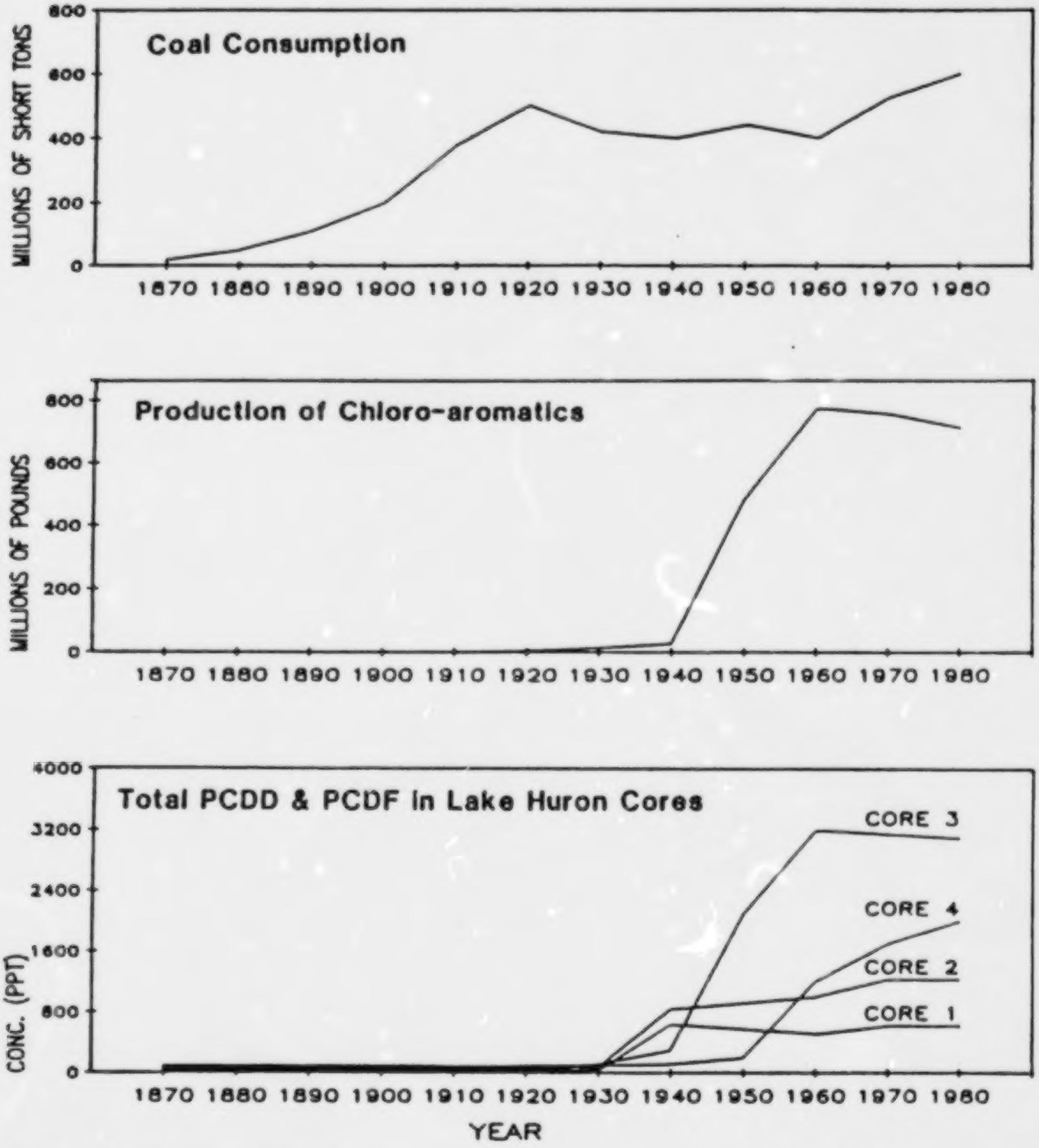
Czuczwa and Hites (1986) have looked extensively at deposition of chlorinated dioxins and dibenzofurans in the Great Lakes particularly in Lake Huron. PCBs in Lake Huron biota show a slowly declining trend. Levels are sharply increased in Saginaw Bay near Midland Michigan and the outflows of the Tittibawasi and Saginaw Rivers. Increasing deposition rates were shown for total PCDDs and PCDFs in Lake Huron which correspond temporally with the production of chloro-aromatics and correspond spatially for PCBs with the proximity to Saginaw Bay and the Saginaw River system. (Figure 3). The types and patterns of chlorinated dioxins and furans corresponded to that coming from combustion of chloroaromatics.

### 2.2.6 ST. CLAIR RIVER

The most recent and striking example of current discharge of waste contaminated with PCDDs and PCDFs is the St. Clair River at Sarnia, Ontario (Canada-Ontario Board of Review, 1985). In this case a large, heavier than water mat or "blob" of chemicals was

Figure 3

U.S. Consumption of Coal and Production of Synthetic Chlorinated Organics Compared to the Total PCDD and PCDF in the Four Lake Huron Cores.



Notes: includes chloro- and dichloro-benzenes, 2,4-dichloro- and 2,4,5-trichlorophenoxyacetic acid, esters and salts, and pentachlorophenol

Source: Czuczwa and Hites, 1986.

found on the bottom of the Canadian side of the river in both 1984 and 1985. This material contained percentage levels of perchloroethylene, part per thousand levels of chlorobenzenes, hexachlorobutadiene, chloropropenes, octa-chlorostyrene, and PCBs and parts per billion levels of PCDDs and PCDFs. Although the octa and heptachlorocongeners of PCDDs and PCDFs predominated, tetrachlorodioxins characteristic of 2,4-D were found. The presence of water soluble compounds such as chloropropenes, chlorobenzenes, and perchloroethylene at extremely high concentrations posed the greatest immediate threat to drinking water supplies. However the less water soluble dioxin/-dibenzofuran residues pose the greatest long-term threat in that they persist in sediment at part per billion levels along approximately a 3 km stretch of the river bottom both upstream and downstream of the tarry mat of chemicals. Candidate sources of this discharge of chemicals which are no longer manufactured by local industry include an industrial landfill, old sewer lines and groundwater contaminated by previous deep well injection of similar wastes. Much of this tarry material was vacuumed from the river bottom during the fall of 1985 and is currently stored in a lagoon near the landfill.

## 2.3 WIDESPREAD TRENDS IN WILDLIFE AND FISH

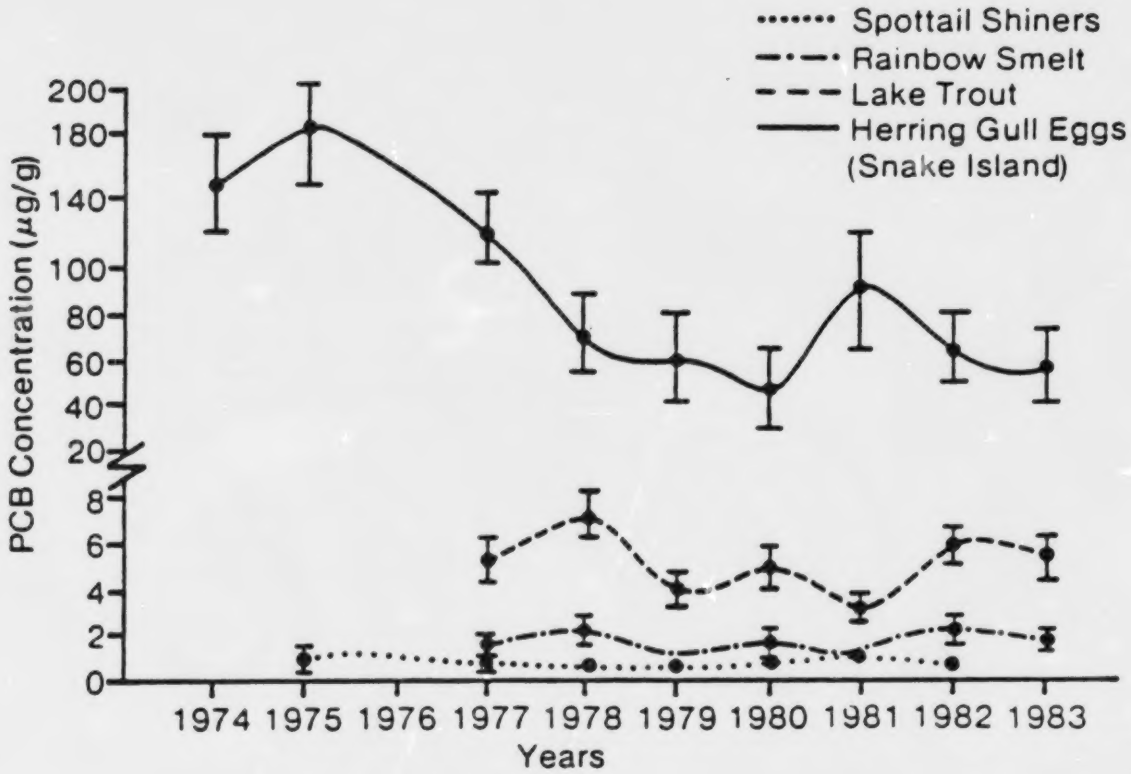
Polychlorinated biphenyls may best exemplify widespread trends of persistent chemicals which are, or are contained in special waste since long-term data bases are available, and their environmental properties are typical of other persistent contaminants. Other contaminants which follow similar trends to PCBs for which data are available include chlorinated benzenes, chlorinated styrenes, and 2,3,7,8 TCDD (Mineau et al, 1985).

The results of studies of PCB concentrations in herring gulls (Struger et al. 1983), lake trout, rainbow smelt (Whittle 1981, 1982; CWS 1985) and spottail shiners (MOE 1982) of Lake Ontario are summarized in Figure 4. Although an initial decline in PCB levels was demonstrated from 1974 to 1979 indicating a net removal of PCBs from the ecosystem, recent trends from 1980 to 83 show little or no decline and indicate that there is no longer a net removal of PCB sources in this ecosystem.

While levels of PCBs in gull eggs of Lake Ontario have decreased rapidly over the decade 1974-1984, herring gull eggs from Lakes Superior and Huron have not shown the same significant decrease in that time (Figure 5, and 6). The trend is toward a more uniform level of PCBs throughout the industrialized and non industrialized Great Lakes. A slowly declining trend is evident throughout the Great Lakes basin. PCB concentrations in lake trout from the same two lakes have declined from 6.14 ug/g in 1978 to 4.59 ug/g in 1983. Since only 3 or 4 years of rainbow smelt data are available for most of the lakes no trend was established. While a general decrease in PCB levels in biota of Lakes Ontario and Huron is seen, lake trout and rainbow smelt of Lake Superior have shown an increase in PCB contamination

**Figure 4**

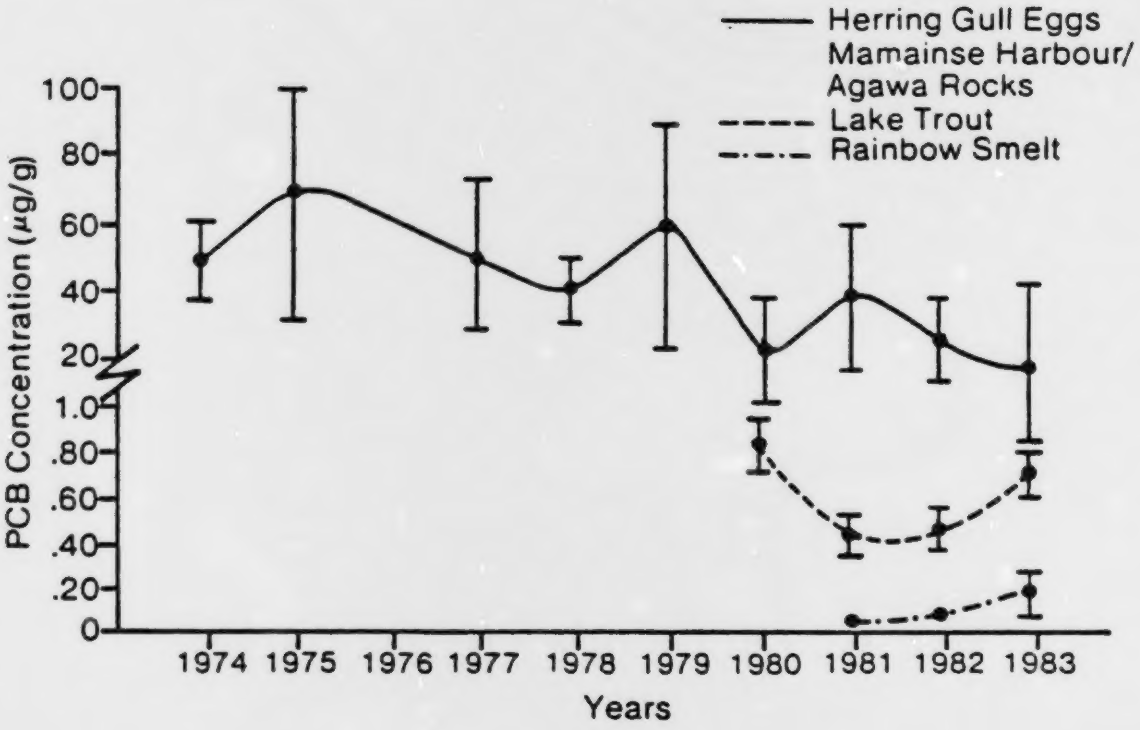
PCB Concentrations in
Lake Ontario Biota



**Source:** Hallett, 1986a.

Figure 5

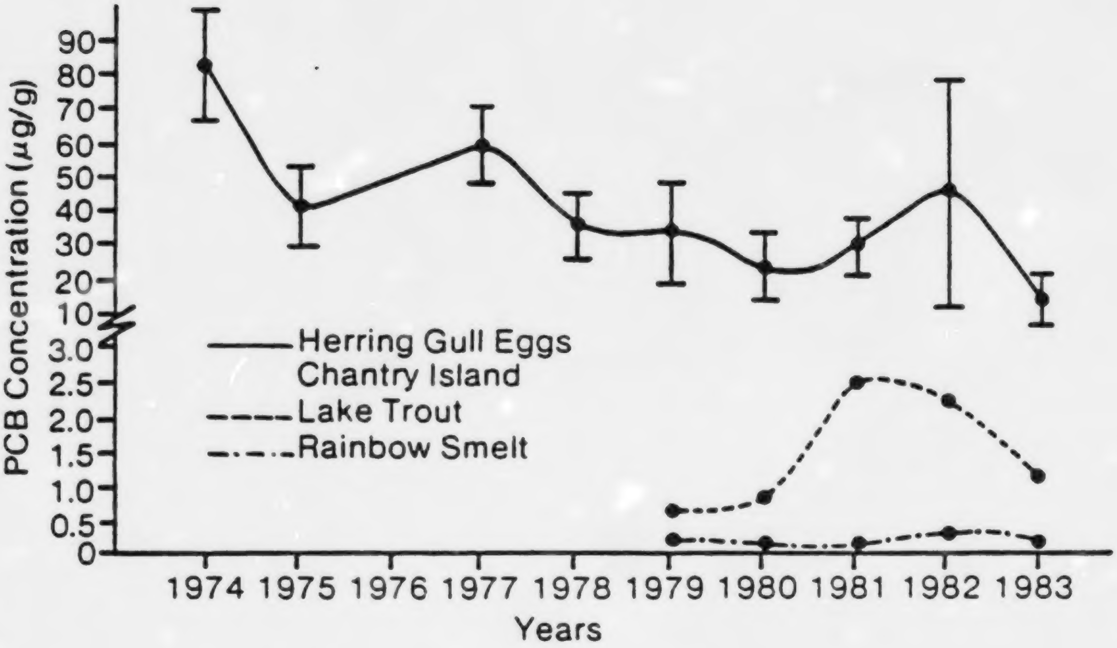
PCB Concentrations
in Lake Superior Biota



Source: Hallett, 1986a.

## Figure 6

PCB Concentrations
in Lake Huron Biota



Source: Hallett, 1986a.

since 1981 indicating increasing deposition of PCBs from unknown sources.

## 2.4 WHY ARE THESE TRENDS OCCURRING?

### 2.4.1 THE ATMOSPHERE

The data with respect to biota and water indicate that residue levels of persistent toxic substances such as PCBs in the relatively non-industrialized upper Great Lakes are now reaching levels similar to those in the heavily industrialized lower Great Lakes. This is the result of continuing accumulation of PCBs from the atmosphere. There have been a number of studies on the concentrations and deposition of trace organic pollutants from air and precipitation into the Great Lakes. Rural concentrations of atmospheric PCBs have been found to be approximately equal to those over the Great Lakes (Eisenreich et al., 1980). These data are summarized in Table 1.

The dry and wet deposition of airborne PCBs to each of the Great Lakes are shown in Figure 7 (Eisenreich et al., 1980). Wet deposition was defined as that which occurs during a rain or snow event while all other forms of deposition were termed dry. Dry deposition of airborne PCBs was significantly higher than wet deposition for all of the lakes. Both dry and wet deposition of airborne PCBs were significantly higher in the upper Great Lakes, than in the lower Great Lakes region. This is due to the higher

## Table 1

## Atmospheric Concentration of PCBs in Different Environments

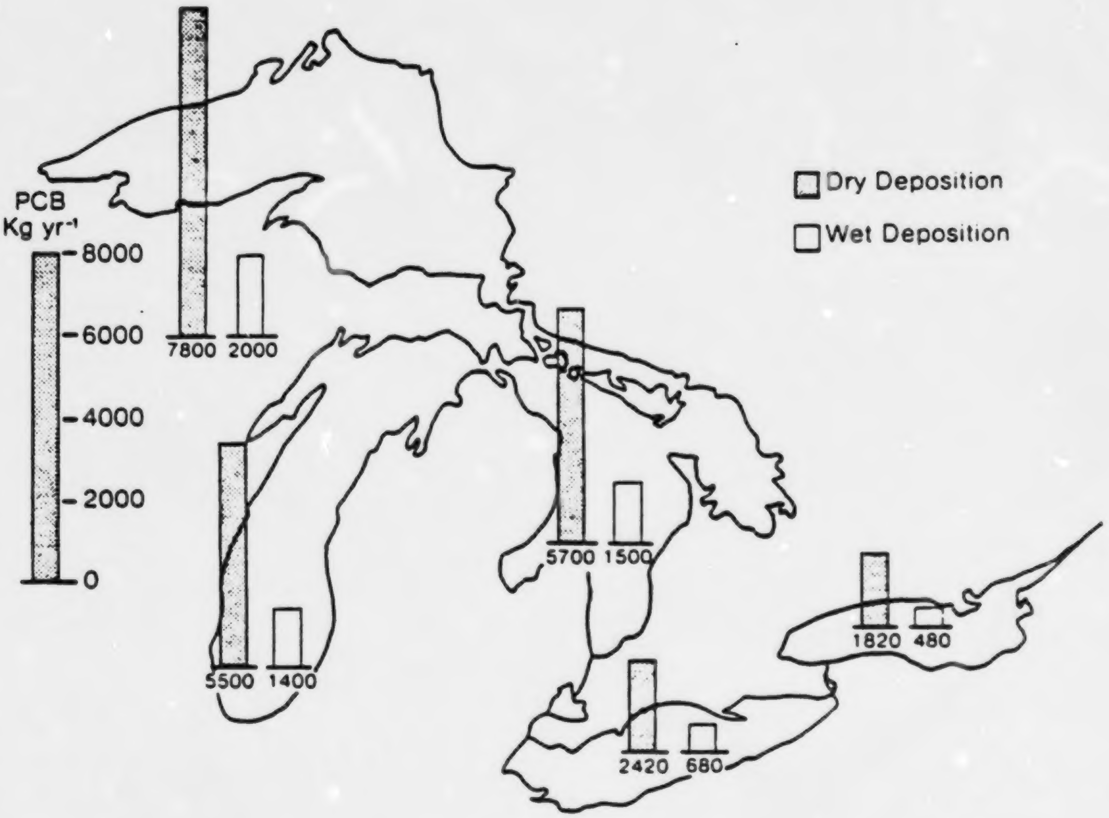
| Location | Vapour & Particulate ($ng/m^3$) |  | Rain & Snow (ng/L) |  |
|---|---|---|---|---|
|  | Range | Mean | Range | Mean |
| Urban | 0.5-30 | 5-10 | 10-250 | 50 |
| Rural | 0.1-2 | 1 | 10-100 | 15-50 |
| Great Lakes | 0.4-3 | 1 | 10-150 | 20-50 |
| Marine | 0.05-2 | 0.5 | 0.5-10 | 1-5 |
| Remote | 0.02-0.5 | 0.1 | 1-30 | 5 |

Source: Eisenreich et al., 1981.

Note: Rural represents non-urban, agricultural or forested areas not adjacent to large water bodies and Great Lakes represents atmospheric measurements taken over or immediately adjacent to the Great Lakes.

## Figure 7

## Dry and Wet Deposition of Airborne PCBs to the Great Lakes


▨ Dry Deposition
☐ Wet Deposition
PCB
Kg yr⁻¹
8000
6000
4000
2000
0
7800
2000
5500
1400
5700
1500
2420
680
1820
480

Source: Eisenreich et al., 1981.

surface areas of the upper Great Lakes allowing for a greater catchment area. The lower Great Lakes however have many more direct sources of PCBs.

Figure 8 details the concentrations of PCBs in rain and snow for areas of the Great Lakes adjacent to Canada (Strachan and Huneault, 1979) and to Lake Michigan (Murphy and Rzeszutko, 1977; Murphy et al., 1980). Significantly higher concentrations of PCBs in rain and snow were found for the area adjacent to Chicago, Lake Michigan. Eisenreich et al. (1980) have also reported higher concentrations of PCBs in precipitation for the Lake Michigan and Lake Superior basins.

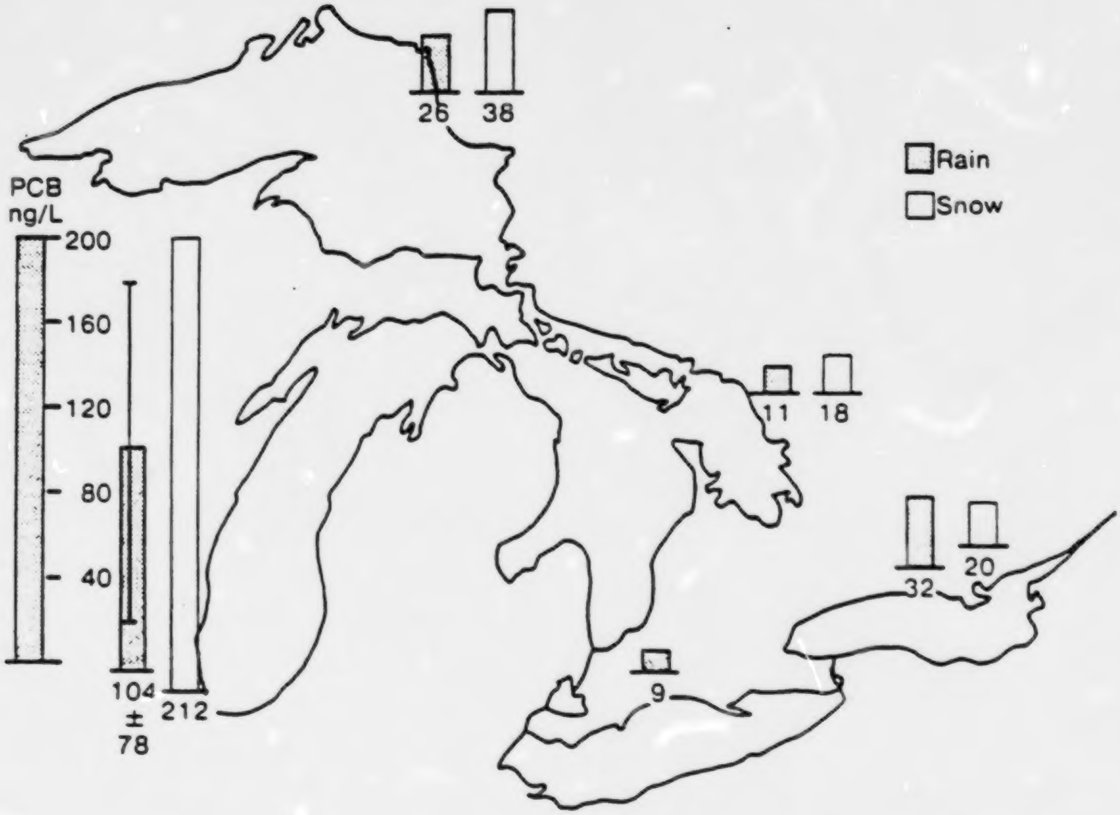
Atmospheric deposition of PCBs to the Great Lakes is the primary input pathway. The results of studies of atmospheric flux of PCBs to the upper relatively non-industrialized Great Lakes suggest that greater than 80% of the total input of PCBs to both lakes is atmospherically derived (Doskey and Andren, 1980; Doskey, 1978; Hollod, 1979; Eisenreich and Hollod, 1980).

### 2.4.2 ATMOSPHERIC INTERACTIONS

Models have been developed to illustrate the movement of PCBs in the ecosystem (Murphy, 1985), (MacKay and Paterson, 1985). These models use the basic chemical properties of chemical compounds to predict their tendency to stay in water, air, or soil. This tendency is termed fugacity. The chemical's vapour pressure is the primary determinant of its tendency to deposit with

### Figure 8

Atmospheric PCBs in the Great Lakes Basin: Rain and Snow 1975-1976.


26
38
Rain
Snow
PCB ng/L
200
160
120
80
40
104 ± 78
212
11
18
32
20
9

Source: Strachan and Huneault, 1979.

precipitation. Lower vapour pressure chemicals such as PCBs are more susceptible to washout in precipitation. Fugacity models also indicate that during precipitation-free periods these compounds volatilize. PCB isomers with three or four chlorine atoms per molecule volatilize at the fastest rate. Thus, cycling of PCBs between air and water is demonstrated. This is of particular concern for the Great Lakes because frequent lower temperatures reduce vapour pressure which increases the chemicals' tendency to condense and therefore to fall out of the atmosphere as precipitation. Compounds used in warmer climates to the south of the Great Lakes such as toxaphene may be deposited preferentially in cooler areas to the north.

### 2.4.3 MASS BALANCE MODELS

An input-output model for PCB cycling in Lake Superior has been constructed by Hollod (1979) and Eisenreich and Hollod (1980). As seen in Table 2, atmospheric deposition represented greater than 85% of the total input to the lake, with tributary inputs primarily contributing to the balance. Losses to the sediment were estimated by adding the measurements of PCB fluxes to the sediment in different sedimentation regions over the whole lake. Tributary outflow represented about 10% of sedimentary losses based on a whole lake concentration of 2 mg/L. Biological

## Table 2

Input-Output Model of PCBs in Lake Superior.

kg/a

| Input | | Output | |
|---|---|---|---|
| Atmosphere | 6600-8300 | St. Mary's River | 140 |
| Tributary | <1311 | Sedimentation | 1000-1600 |
| Municipal | 66 | Degradation | ? |
| Industrial | 2 | Water-Air Transfer | ? |
| Total | 8000-9700 | Total | 1140-1740 |

Source: Eisenreich et al., 1981.

degradation is not considered to be an important loss mechanism since higher molecule weight isomers are resistant to biological degradation (National Academy of Science, 1979). Water to air transport of PCBs involves the process of aerosolization and volatilization. Limited knowledge about these processes represents a key gap in scientific understanding of ecosystem cycling and mass balance equations related to environmental contaminants.

### 2.4.4 URBAN RUNOFF

Persistent contaminants can also enter the environment through urban run-off. Ubran run-off is storm water which after accumulating metals and organic substances from urban dust and other sources present on streets and in sewer lines is discharged to Ontario waterways. The annual rates of loading of PCBs have been determined in run-off from selected urban areas in the lower Great Lakes Basin (Marsalek, 1983). These results are shown in Table 3. Highly industrialized urban centres such as Hamilton, Toronto and Windsor have the highest estimates of annual loadings of PCBs in urban run-off.

### 2.4.5 SENSITIVITY OF THE GREAT LAKES

The whole ecosystem impact of annual loadings of persistent toxic substances such as PCBs must be considered in each of the

## Table 3

### Estimates of Annual Loadings of PCBs Substances in Runoff from Selected Urban Areas in the Lower Great Lakes Basin

| Urban Area | Loadings in Water (kg/a) | Loadings Attached to Sediment (kg/a) | Water Plus Sediment Loadings (kg/a) |
|---|---|---|---|
| Ajax | 0.04 | 0.87 | 0.92 |
| Belleville | 0.10 | 1.84 | 1.93 |
| Brampton | 0.29 | 9.13 | 9.42 |
| Brantford | 0.19 | 4.86 | 5.05 |
| Burlington | 0.26 | 5.63 | 5.89 |
| Cambridge | 0.18 | 2.97 | 3.15 |
| Chatham | 0.09 | 2.76 | 2.85 |
| Cobourg | 0.03 | 0.45 | 0.48 |
| Cornwall | 0.08 | 1.87 | 1.95 |
| Dundas | 0.05 | 0.74 | 0.79 |
| Etobicoke | 0.65 | 17.42 | 18.07 |
| Fort Erie | 0.04 | 0.80 | 0.84 |
| Halton Hills | 0.06 | 1.32 | 1.38 |
| Guelph | 0.17 | 3.05 | 3.22 |
| Hamilton | 0.63 | 23.14 | 23.77 |
| Kingston | 0.14 | 4.19 | 4.33 |
| Kitchener-Waterloo | 0.47 | 9.66 | 10.12 |
| Leamington | 0.03 | 0.49 | 0.51 |
| Lindsay | 0.04 | 0.54 | 0.58 |
| London | 0.67 | 11.94 | 12.61 |
| Markham | 0.09 | 2.49 | 2.58 |
| Mississauga | 0.55 | 13.79 | 14.34 |
| Newmarket | 0.07 | 1.27 | 1.34 |
| Niagara Falls | 0.17 | 3.88 | 4.05 |
| Oakville | 0.17 | 3.44 | 3.61 |
| Oshawa | 0.30 | 7.53 | 7.83 |
| Peterborough | 0.15 | 2.27 | 2.43 |
| Pickering | 0.07 | 1.29 | 1.35 |
| Port Colbourne | 0.06 | 0.72 | 0.78 |
| Richmond Hill | 0.09 | 1.55 | 1.64 |
| St. Catharines | 0.29 | 8.59 | 8.88 |
| St. Thomas | 0.07 | 1.22 | 1.29 |
| Sarnia | 0.12 | 3.64 | 3.76 |
| Scarborough | 0.85 | 26.86 | 27.71 |
| Simcoe | 0.03 | 0.56 | 0.59 |
| Stratford | 0.08 | 1.00 | 1.08 |
| Toronto | 0.84 | 24.43 | 25.27 |
| Trenton | 0.04 | 0.56 | 0.60 |
| Wallaceburg | 0.03 | 0.50 | 0.52 |
| Welland | 0.12 | 1.95 | 2.07 |
| Whitby | 0.07 | 1.22 | 1.29 |
| Windsor | 0.45 | 10.82 | 11.27 |
| Woodstock | 0.08 | 1.03 | 1.10 |
| York | 0.19 | 5.94 | 6.13 |
| York, East | 0.16 | 5.03 | 5.19 |
| York, North | 1.14 | 33.89 | 35.03 |
| Total | 10.50 | 269.10 | 279.60 |

Source: Marsalek, 1983

individual Great Lakes ecosystems. Each of the Great Lakes and particularly the large deep Upper Great Lakes of Superior, Michigan and Huron are extremely sensitive to loadings of persistent toxic chemicals due to their long flushing time. The flushing time to remove 50% of a conservative material from Lake Superior is 120 years, reaching to 500 to remove 95% of the material (Bennett, 1978). Lake Huron including Georgian Bay has a total flushing time of 50 years as does Lake Michigan (Rainey, 1967). Flushing time of Lake Erie is 2.5 years (Sly, 1976), and Lake Ontario approximately 7 to 10 years (Rainey, 1967). Therefore when a persistent substance enters one of these lakes it will take many years to remove it.

## 2.5 MAJOR CHEMICALS OCCURRING IN ONTARIO BIOTA

### 2.5.1 INTRODUCTION

In sections 2.3 and 2.4 PCBs and chlorinated dioxins have been highlighted since they are well studied high hazard compounds derived from special waste. Extensive long-term data bases are available for PCBs. In this section the other priority chemicals found in the Great Lakes and in Ontario biota are briefly described. The following series of chemicals and descriptions were developed by the federal Interdepartmental Committee on Great Lakes Toxic Chemicals (GLTCC, 1985) between 1982 and 1986 as the focus for program development. This section is presented here to briefly overview the other major toxic chemical problems as seen by federal scientists.

### 2.5.2 CHLORINATED DIBENZODIOXINS AND FURANS

Chlorinated dibenzodioxins became a Great Lakes concern in 1979 when 2,3,7,8-TCDD was discovered in fish from Lake Ontario and from tributaries entering Saginaw Bay, Lake Huron. During 1980, some measure of the geographical distribution of 2,3,7,8-TCDD within the system was obtained using the eggs of the herring gull. Areas of high contamination were identified as Lake Ontario, Saginaw Bay and the Detroit River; the Niagara River was implicated as a point source for the first site and the Tittibawasi River for the second and third (Mineau et al., 1985). Limited data are available on the other chlorinated dibenzodioxins and furans which are also present on a widespread basis with higher concentrations near industrial centres. More recently, these compounds have been noted in mothers' milk in other areas of the world (Rappe, 1986). Health & Welfare Canada has reported chlorinated dioxins and dibenzofurans in human adipose tissues from cadavers across Canada (Ryan et al., 1985).

### 2.5.3 ALKYL LEAD COMPOUNDS

Alkyl lead compounds are highly toxic, readily bioavailable and have been found in aquatic biota from several Great Lakes locations related to known industrial sources of these chemicals. There are two known sources of alkyl lead compounds in the Canadian Great Lakes - the Ethyl Corp. at Sarnia on the St. Clair River, and Dupont of Canada at Maitland on the St. Lawrence River. As well, the Niagara River Toxic Chemicals Committee Report suggests that there are large amounts of these chemicals in dumps in the Buffalo/Niagara Falls area (NRTC, 1984). High levels of alkyl leads occur in St. Lawrence River biota downstream of the Dupont plant and lesser amounts occur in fish near the St. Clair River site. Alkyl lead is found in fish fillets of all species caught near the outfalls of these two plants. Remedial work is underway at the Maitland location. Human health effects of ingested alkyl leads are unknown and fish consumption guidelines have not been described. Some alkyl lead compounds are 10-100 times more acutely lethal than inorganic lead.

### 2.5.4 TOXAPHENE IN THE UPPER GREAT LAKES

Toxaphene is an organochlorine pesticide which is not used widely in Ontario and is not a special industrial waste. However toxaphene demonstrates the importance of atmospheric transport of persistent environmental contaminants including PCBs or chlorinated benzenes and the sensitivity of the Great Lakes to this pathway. Toxaphene has been used extensively in the southeastern United States in aerial spray programs. It is possible that, in addition to the direct input to the atmosphere, volatilization of the pesticide from the soil may act as a long term atmospheric source. Although it has been used only slightly in the Great Lakes basin, this pesticide has been observed in fish from most of the Great Lakes. Long range atmospheric transport and deposition is implicated as the source to the Great Lakes. Toxaphene is a complex mixture of organochlorine compounds whose structures suggest high persistence, accumulation and sub-lethal toxicity. From 1972 and 1984 lake trout from all lakes in the system approached the U.S. food guidelines and that levels in predator fish from the upper Great Lakes were at or above those levels associated with adverse effects observed in the laboratory. Skeletal abnormalities in the same fish studied in the laboratory have been suggested as deriving from toxaphene (Rice and Evans, 1985).

### 2.5.5 POLYCHLORINATED DIPHENYL ETHERS (PCDE)

In a preliminary survey of biological and sediment samples from the Great Lakes, PCDEs were indicated as trace contaminants throughout Lake Ontario and in Whitby Harbour in particular. A recent monitoring study of twenty fish samples from Lake Ontario and the St. Lawrence River indicated levels of 0.2-8.2 ppm (pers. comm. D. M. Whittle, Dept of Fisheries and Oceans). Earlier work had established that Whitby Harbour sediments were contaminated with these compounds. Possible sources for Lake Ontario are industrial effluents from heat transfer systems which have undergone chlorination in the waste treatment process. Other sources include the discharge or leaching of PCDE contaminated chlorinated phenols as well as improper incineration of wastes. The PCDEs are acutely toxic to fish at low concentrations (increasingly so with increasing degree of chlorination). They bioaccumulate and induce enzyme systems in mammals. Experimental data on uptake, elimination, partitioning and toxicity indicate that PCDEs have similar properties to other environmental contaminants of concern such as PCBs and HCB. PCDEs may also be converted to the corresponding dibenzofurans by irradiation with UV light and to the dibenzodioxins by combustion (pers. comm. D. M. Whittle, Dept. of Fisheries and Oceans).

### 2.5.6 POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) AND HETEROCYCLIC AROMATIC HYDROCARBONS (HAC).

The type of sources of PAHs and HACs and their detection in the aquatic environment suggests that they are widespread and that organisms are continuously exposed to them, albeit at largely unknown concentrations. HACs are less well documented in the Great Lakes than are PAHs.

PAHs and HACs are well-defined constituents of fossil fuels and the combustion products of such fuels; they are also products in the combustion of most plant materials. They are particularly prevalent around coking operations associated with iron and steel production such as Sault Ste Marie, the Detroit River, the Niagara River, and Hamilton Harbour and in this case are constituents of the special waste derived from these industries (Hallett and Brecher, 1985). Many of these same compounds have been shown to be carcinogenic to humans. Organisms above the insect/invertebrate level readily metabolize PAHs but very little is known of the fate and effects of the breakdown products. (It is known that they are involved in carcinogenic tumour induction in mammals and fish, however). In the aquatic environment, little is known of any sub-lethal effects of chronic exposure to organisms resident there, although induction of tumours in bottom feeding fishes has been reported under laboratory conditions (Hallett and Brecher, 1985).

### 2.5.7 SELENIUM

Selenium (Se) is an essential nutrient at low levels but is toxic at higher concentrations. Furthermore, Se typically has an antagonistic effect on the toxicity and bioaccumulation of toxic metals, particularly mercury, arsenic, copper, lead and cadmium. Selenium levels in the Great Lakes are generally low but some contamination of zooplankton has been observed in Lake Michigan downwind of Chicago and in fish from Georgian Bay/North Channel

High selenium levels in the rocks and soils of the watershed north of Georgian Bay may be the source in the latter case. Laboratory and field studies of selenium cycling and effects in aquatic ecosystems have shown that sediments adsorb selenium, that benthos may accumulate Se and that levels in benthos in excess of 5-10 ug/g (ppm) are lethal to predatory fish (Hodson, Whittle, and Hallett, 1985).

### 2.5.8 CHLOROPHENOLS

Substantial pentachlorophenol (PCP) discharges were noted in the mid-1970's in sediments and fish at Thunder Bay (Lake Superior) and at Trenton (Bay of Quinte, Lake Ontario). Wood treatment plants are likely sources. Municipal sewage outlets were another identified source type, particularly at the mouth of the Detroit River and in Hamilton Harbour. Chlorophenols generally are observed in the Niagara River area. Trichloro-, tetrachloro- and pentachloro-phenols and wastes from their production are direct sources of both chlorinated dioxins and chlorinated dibenzofurans.

PCP is a broad spectrum biocide which can be persistent under some circumstances, notably the anaerobic (oxygen-free) conditions often found in sediments. Other chlorophenols, while generally less persistent, are also biocides and may survive long enough in the aquatic environment to cause an effect.

### 2.5.9 MERCURY

Historically, two major sites of mercury contamination were identified on the Canadian side of the Great Lakes - at Penninsula Harbour (Marathon, Lake Superior) and on the St. Clair River (at the Dow Chemical plant in Sarnia). The Wabagoon-English River system near Dryden, Ontario was similarly affected.

Both sites (Marathon and Sarnia) were locations for the production of chlorine using the mercury electrode process and at both there were substantial losses of metallic mercury, some of which was ultimately methylated in the sediments. In the St. Clair River, the sediment and fish concentrations of mercury were observed to move downstream into and through the western basin of Lake Erie. Levels were such that the fishery in Lake St. Clair was closed. At Peninsula Harbour, the embayment waters and sediment do not exchange readily with the lake and fish and sediment levels are still found to be high (I.J.C., 1985b).

### 2.5.10 POLYCHLORINATED STYRENES (PCS)

Octachlorostyrene (OCS) and two of the heptachlorostyrene isomers have been detected in fish and herring gulls of the Great Lakes. Their structural similarities to the PCBs suggests high persistence, accumulation and sub-lethal toxicity. Sources which have been implicated include municipal incinerators and industrial plants using older type carbon electrodes and chloride solution in electrolysis processes (I.J.C., 1985b). It is also probable that other congeners from the PCS series are formed.

These compounds have been found at ppm levels in fish at several locations within the Great Lakes ecosystem. They have been reported at elevated levels near the Dow plant at Sarnia. PCSs have also been reported as being produced in incinerators of solid wastes. Indications are that they persist and that they bioaccumulate.

### 2.5.11 POLYCHLORINATED BIPHENYLS (PCB) AND ORGANOCHLORINE PESTICIDES (OC)

Elevated levels of some OCs and PCBs are still found in the Great Lakes, particularly in the biota, which result in continued restrictions and advisories on fish sale and consumption. Evidence has recently come to light that the decline in these levels observed up to 1980 is not continuing as expected (I.J.C., 1985b). This may lead to long-term effects on the biota and to an indefinite continuation of the above controls.

In general, residue levels of measured OCs and PCBs in the Great Lakes system have declined since such analyses began in the 1970's; however, all lakes still exhibit fish populations with residue levels exceeding the 1978 Great Lakes Water Quality Agreement objectives. Declining levels which were apparent in herring gull eggs and some species of fish have apparently leveled out since 1980 and may even be increasing again. In the case of PCBs and DDT, severe restrictions have been in place for nearly ten years, yet these substances continue to be found in substantial quantities in rain, sediments, air and biota.

Compounds found and for which objectives exist under the Great Lakes Water Quality Agreement include PCBs, lindane, aldrin/dieldrin, chlordane, DDT and metabolites, endrin, heptachlor/heptachlor epoxide, methoxychlor, mirex, toxaphene, pentachlorophenol and polychlorinated dibenzodioxins.

### 2.5.12 PESTICIDES

Because of their intrinsically high biocidal and often persistent nature, pesticides have the potential to significantly degrade the quality of Ontario waters. Pesticides are used extensively in the Great Lakes basin and elsewhere in North America. Some of these have been shown to contaminate the Great Lakes ecosystem through processes of spray drift, vapour transport, runoff and groundwater movement from sites of use in Ontario; contamination by long range atmospheric transport from sites outside Ontario also occurs.

Over 500 active ingredients are registered for use under the Pest Control Products Act of Canada. Their uses are further restricted through licensing and permit provisions imposed by the

Province of Ontario. Many of these active ingredients were registered prior to 1970-75 on the basis of scientific and technical data that are now considered inadequate to ensure environmental and human safety. These "old" pesticides require reassessment of their fate and effects under actual use conditions as well as through modern testing practices.

The Pollution from Land Use Activities Reference Group's report to the International Joint Commission (PLUARG, 1982) demonstrated the importance of the potential for contamination of water adjacent to agricultural areas and the cumulative impacts that these local sources could have on total Great Lakes loading of pesticides.

## 2.6 DISCUSSION

Long-term trends in toxic chemical contamination where available in environmental indicators have shown substantial decreases on a local basis in severely contaminated industrial areas such as the Niagara River. However, long-term trends of the same contaminants on a more widespread basis show very slow declines such as those for Lake Superior. Current trends have also slowed their decline and in some areas such as Lake Ontario increases are evident for contaminants such as chlorinated dioxins. The major reason for this phenomenon is the persistence of many industrial contaminants which allows cycling and a gradual spreading of the contaminant problem through either atmospheric or aquatic dispersal. In-situ sources from previous contamination due to inadequate disposal practices such as contaminated harbour sediments now act as continuous sources to the water column. These continuous in-situ loadings are likely slowing the decline of residues evident in fish and wildlife in the Great Lakes ecosystem. The lower input of contaminants into the lakes today likely has a more severe impact since this loading is now additive to the continuous loading from the in-situ sources.

During the 1970s, toxic chemicals that were environmentally persistent became an international concern. This was due not only to their ability to bioaccumulate and bioconcentrate in aquatic and terrestrial food chains to toxic levels but also to their ability to persist, cycle, and travel within the five compartments of the ecosystem; the air, water, soil, sediment and biota. Effective management practice should not simply remove the problem substance from one compartment of the ecosystem, but effectively remove it once and for all from all compartments. In addition, dilution of such substances in effluents to meet "non-toxic" concentrations simply allows the same continuous loading of these persistent compounds resulting in accumulation in the lakes. Contaminant levels, on a local and widespread basis, are declining very slowly, if at all, because of the continued loading of residues into the ecosystem from industrial and municipal sources as well as in-situ sources such as contaminated harbour sediments. These trends indicate that at present the loading rate of these compounds into the Ontario Great Lakes, and the global ecosystem is too high for the ecosystem to remove them quickly into the relatively terminal sinks such as deep lake and ocean sediments. Residues remain in the ecosystem long enough for bioaccumulation to occur up food chains. Widespread declines are therefore not evident in biota. The current loading rates of these chemicals must be reduced to lessen the impact.

## 2.7 MAJOR FINDINGS

1. Current Trends of Toxic Chemicals in the Ontario Environment.

a) Of the major environmental contaminants which are found in the Ontario environment the majority are derived from persistent industrial chemicals found in special waste, and as combustion products in municipal incinerators with the rest resulting from the application, primarily in the past, of hard pesticides such as DDT which biodegrade very slowly (see section 2.5).

b) The contaminants which are found are present because of their environmental persistence, their ability to bioaccumulate, and the prevalence of their sources.

c) The Ontario ecosystem, is particularly susceptible to persistent toxic chemicals because of the retention time of the Great Lakes, and the propensity of these compounds to cycle between the large bodies of water and the atmosphere. In addition, these lakes are now particularly sensitive because large in-situ areas of contaminants, which have built up over the past 40 years, now act as continuous sources to the water column.

d) The atmosphere has become the major pathway of transport for persistent toxic chemicals to Ontario land and water.

e) Localized and widespread trends of environmental contaminant levels show rapid declines during the period from 1970 to 1980 which are likely due to the initial legislation which restricted the chemical manufacture or usage of certain compounds such as DDT or PCBs; the better industrial treatment of aquatic effluents; and the reduction of gross toxic chemical pollution which was evident in the Niagara River about 1960.

f) Since 1980, although many localized trends of environmental contaminants continue to show a decline, widespread trends such as whole lake trends of certain environmental contaminants in Lake Ontario have become stationary while others show an increase. In other areas such as Lake Superior marginally slow declines continue.

g) The increases and slowly declining trends are evidence of continuing environmental sources of persistent chemicals derived from sources including special waste. These chemicals are entering the Ontario ecosystem at a rate which is slightly more or less than the rate by which they are being effectively removed from circulation. Exposure of biota including humans is caused by the continuing circulation of the contaminants within the ecosystem.

# CHAPTER 3

# IMPACT ON FISH AND WILDLIFE FROM THE MAJOR TOXIC CHEMICALS ORIGINATING FROM SPECIAL WASTE IN ONTARIO

## 3.1 INTRODUCTION

Many chemicals present in special waste have been assessed to be toxic because they cause effects in many laboratory organisms. However it is often difficult to translate laboratory toxicology to the real world where multiple levels of ecosystems are exposed to many chemicals simultaneously.

Ontario fish, fish-eating mammals and birds, and other wildlife have been the subject of many scientific studies to determine detrimental impacts as they occur in populations, individual organisms, and even specific organs within individuals. The following chapter describes the studies which show the "real-world" effects which have occurred and unfortunately still are occurring in the Ontario environment caused by persistent toxic chemicals of anthropogenic origin.

## 3.2 THE POPULATION PERSPECTIVE

Persistent toxic chemicals from special waste are seldom outright or acute killers of either fish, wildlife or humans at levels found in the environment. Effects are seldom demonstrated at lower levels of the food web as they are chronic in nature and difficult to determine. Chronic effects include immuno-suppression, (decreasing the ability of an organism to combat disease), neural depression, lowered fertility, etc.

Multiples of these chronic effects manifest into more obvious problems for individuals. Reproduction may be totally impaired due to eggshell thinning or teratogenic effects. Cancer can be caused by either direct induction by genetically active chemicals or cancer can be promoted by the sum total of many effects from the same or other chemicals and other diseases. Some individuals are predisposed to the effects of toxic chemicals biochemically, and for humans, by social habits such as smoking or alcohol consumption, or by exposure to other chemical promoters found in the workplace or home.

Reality becomes harsh when individual effects begin to add up in populations of a single species to the extent that a whole population declines or disappears. The demonstration of population-level effects must be considered a very grave situation. If one population level in an ecosystem changes, the once stable ecosystem may quickly undergo an irreversible catastrophic change especially if a keystone species population is lost. In addition, when population-level effects are caused by toxic chemicals, individuals from the most sensitive and the more highly exposed, to the least sensitive, and only occasionally exposed, are all being affected and will continue to be affected until the source of the chemical exposure is stopped and until the latent effects subside.

This lag phase or latency period between chemical cause and chronic illness showing up at the population level has been difficult to record and document scientifically. This is due to the large numbers of subjects and long length of time which must span several generations necessary for these studies. The most striking long term dataset of such a population effect is the increasing rate of lung cancer in North American male and female humans corresponding to the increase in rate of smoking. The rate of cancer in males then decreased as the rate of smoking subsided (Figure 9). There is a distinct lag phase of 10 to 15 years between the cause ie. rate of smoking, and the effect ie. rate of lung cancer.

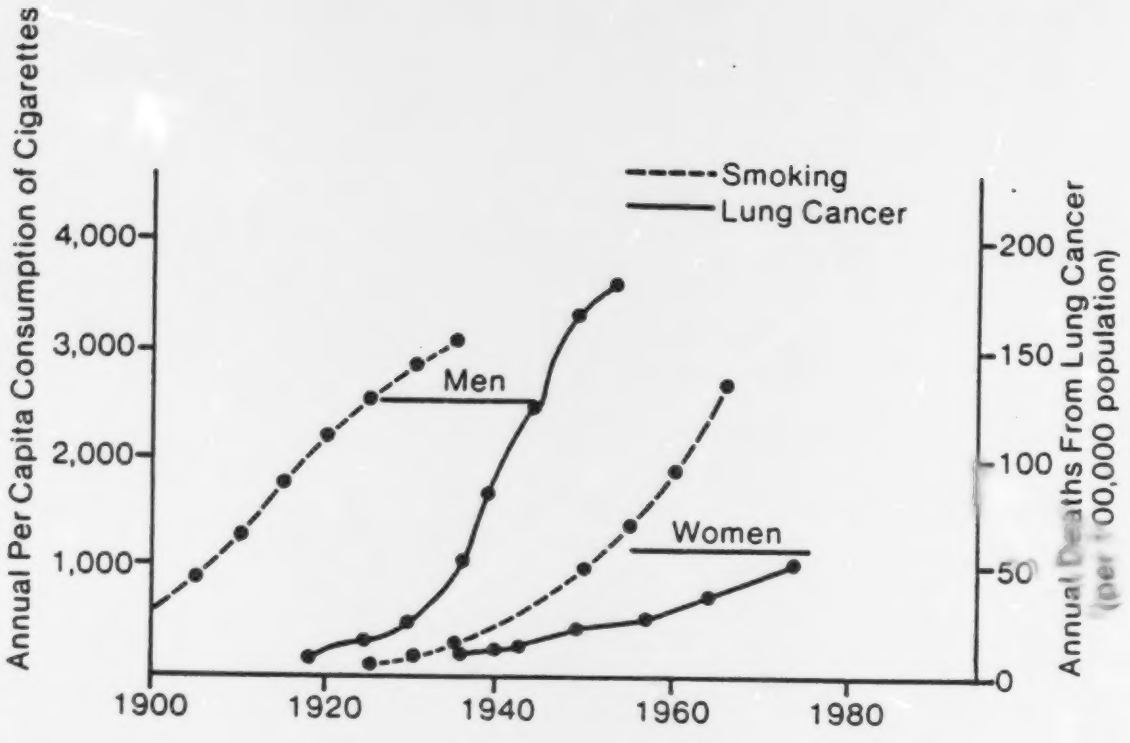
The following sections will discuss in detail toxic chemical associated population-level effects observed in fish-eating birds, mink, Beluga whales and fish in the Great Lakes ecosystem.

## 3.3 CHRONIC EFFECTS OF PERSISTENT TOXIC CHEMICALS IN ONTARIO FISH-EATING BIRDS

The longevity of fish-eating colonial-nesting waterbirds and their ability to bioconcentrate persistent toxic chemical residues from their food, allows them to be model "populations at risk" in which to study chronic toxicity in a "real-world"

## Figure 9

Smoking and Lung Cancer



Source: Cairns, 1975.

situation. Fish-eating water birds resident on the Great Lakes such as herring gulls, common terns, Forsters terns, double-crested cormorants, black-crowned night herons, ospreys and bald eagles (Table 4) have exhibited population effects resulting from eggshell thinning, embryo toxicity, teratogenicity and behavioral deviations (Peakall, 1986). These have all been demonstrably caused by persistent organochlorine chemicals derived from special waste save for DDT. Organ-level effects which have been observed in these birds include thyroid hyperplasia (goiter), hepatic porphoryia (liver disease) and effects on mixed function oxidases of the liver (key liver function enzymes). These effects are detailed in following sections of this chapter.

It has been shown that persistent toxic chemicals such as PCBs are bioconcentrated in herring gull eggs 25 000 000 times the ambient concentration in lake water (Norstrom et al. 1978), and approximately 20x that of predator fish such as coho salmon. This is due to the fact that most persistent organic residues of concern in special waste are lipophilic or fat-loving which promotes bioaccumulation through food chains and bioconcentration in lipid (fat) rich eggs. This results in relatively high exposures to these residues at the very susceptible embryonic stage. Scientifically, effects and residue levels are more easily measured and correlated in these species for the same reasons.

## Table 4

## Species of Fish-Eating Birds Affected by Pollutants in the Great Lakes of North America

| Species | Effects seen |
|---|---|
| Double-crested Cormorant<br>(Phalacrocorax auritus) | Population decline<br>Reproductive failure<br>Eggshell thinning<br>Congenital anomalies |
| Black-crowned Night Heron<br>(Nycticorax nycticorax) | Population decline<br>Eggshell thinning |
| Bald Eagle<br>(Haliaetus leucocephalus) | Population decline<br>Eggshell thinning |
| Osprey<br>(Pandion haliaetus) | Population decline<br>Eggshell thinning |
| Herring Gull<br>(Larus argentatus) | Reproductive failure<br>Behavioural effects<br>Biochemical changes<br>Congenital anomalies |
| Common Tern<br>(Sterna hirundo) | Reproductive failure<br>Congenital anomalies |
| Forster's Tern<br>(Sterna fosteri) | Reproductive failure<br>Behavioural effects<br>Congenital anomalies |

Source: Peakall, 1986

### 3.3.1 EGGSHELL THINNING

Reproductive failures in many avian species as a result of eggshell thinning, flaking eggshells, and dented or collapsed shells have been shown experimentally to be caused by high residue levels of DDE which is the terminal metabolite of DDT, an organochlorine pesticide which was restricted in use in North America about 1970. Residues of DDE and DDT are still prevalent because of the environmental persistence of DDE, the continued leaching of DDT from industrial landfills associated with its manufacture, and the use of DDT in newer pesticide formulations.

Severe eggshell thinning was the cause of the reproductive failure and associated population decline of double-crested cormorants in the Great Lakes (Table 5). In the early 1950s declining numbers of breeding cormorants were observed in Lake Michigan and by 1963 nesting was no longer observed. By the early 1970s breeding was no longer observed on Lake Superior and had been reduced by 80% on Lake Ontario. Eggshells on the Great Lakes were 30% thinner than normal and 79% of the eggs had broken or had disappeared within 8 days of laying (Weseloh et al., 1983). Since this period, eggshell thickness has increased in response to the declining levels of DDE found in the food chain since the restrictions on usage in North America. The breeding population has expanded as it has been experiencing normal reproductive success since the late 1970s.

The population of [illegible]k-crowned night herons also nesting on Pigeon Island declined by 80% during the 1960s. Eggshells measured during the early 1970s were 12 to 17% thinner than

## Table 5

## Population Size and Productivity of the Double-crested Cormorant in the Great Lakes, 1972/73 and 1979/81.

| | 1945/50 | 1972 | 1973 | 1979 | 1980 | 1981 |
|---|---|---|---|---|---|---|
| Lake Ontario | 200-240 | 10<br>(0) | 3<br>(0) | 40<br>(nd) | 99<br>(0.9-1.7) | 180<br>(1.4-1.5) |
| Lake Erie | 22 | 46<br>(0.5) | 39<br>(0.9) | 87<br>(2.4-3.2) | 114<br>(1.8-2.0) | 148<br>(1.7-1.9) |
| Lake Huron | 400 | 66<br>(0.06-0.14) | 58<br>(0.2-1.0) | 202<br>(1.7-2.0) | 335<br>(1.6-2.1) | 392<br>(1.3-2.3) |
| Lake Superior | 120-135 | 0<br>(nd) | 14<br>(0.7-0.8) | 35<br>(nd) | nd<br>(nd) | 190<br>(1.3-1.9) |
| Lake Michigan | 100+ | 0 | 0 | 68<br>(1.3-1.8) | 163<br>(1.6-2.2) | 311<br>(2.0-2.3) |

Productivity (young/nest) figures in brackets.

nd not determined.

Source: Postupalsky (1978), Weseloh et al. (1983), Ludwig (1984).

normal and reproductive success was well below that necessary to maintain population levels (Price, 1976).

Reproductive failures in Great Lakes herring gulls were first noted in Lake Michigan (Keith, 1966, Ludwig and Tomoff, 1966) where thin, flaking eggshells, high embryonic mortality, poor chick survival, and abnormal parental behavior were suggested as causes. These studies on herring gulls began a lengthy investigation which led to the discovery of other contaminants such as PCBs, and chlorinated dioxins since the reproduction problems were not only due to collapsed eggs. Herring gulls are extremely resistant to eggshell thinning.

### 3.3.2 FEMINIZATION AND ABNORMAL PAIRING

A high incidence of nest sharing due to female-female pairing was first observed in herring gulls nesting on Lake Ontario and Lake Michigan in 1977. This phenomenon declined over the next 4 years. Since gulls do not breed until they are at least 4 years old these female-female pairs would have been derived from survivors of the earlier period of high contamination. DDT and its metabolites have been shown to hormonally induce feminization of male embryos rendering them infertile (Fry and Toone, 1981). The high levels of DDT evident in gulls during the early 1970s could be the cause of the observed imbalance in the operational sex ratio of herring gulls in the late 1970s. The effects of other organochlorine residues present such as PCBs, chlorinated benzenes, and chlorinated dioxins have not been studied in this fashion although all are known to affect hormone induction.

### 3.3.3 EMBRYOTOXICITY

Observations on herring gulls on both Lake Michigan in 1966 (Keith, 1966) and Lake Ontario (Gilbertson, 1974, Gilbertson and Hale, 1974) indicated that reproductive failures were not due to eggshell thinning but to embryonic death and egg disappearance. Common tern eggs in Hamilton Harbour were also observed to be dying in the embryonic stages before hatching during 1972-73. The survival of hatched young to fledging or independent feeding and flight was also low. Reproduction was impaired at all possible levels. Artificial incubation of highly contaminated eggs collected in Lake Ontario colonies when compared to relatively clean eggs collected from the Atlantic coast clearly indicated that chemical agents or embryotoxic factors bioaccumulated from the Lake Ontario food chain were responsible for the reproductive failures.

### 3.3.4 BEHAVIORAL TOXICITY

Egg exchanges between contaminated Lake Ontario herring gull colonies experiencing reproductive failures and relatively uncontaminated herring gull colonies not experiencing reproductive failures showed that reproductive failure was not only due to embryotoxic contaminants present in the eggs but was also due to the behavior of contaminated adults who were unable to hatch relatively uncontaminated eggs from colonies experiencing normal reproductive success (Peakall et al. 1980).

Lake Ontario gulls were shown later to be poor parents, being less attentive to their nests, allowing predation of their young by other gulls, and also allowing their eggs to cool.

Currently a similar phenomenon is occurring in Green Bay, Wisconsin with Forster's terns where hatching success is 50% of normal (Harris et al. 1985). Observations are consistent with the previous Lake Ontario herring gull problem with similar high levels of organochlorine chemicals causing both embryonic mortality and less attentive parental behavior to the point of nest abandonment.

### 3.3.5 TERATOGENICITY

During the early 1970s congenital anomalies (crossed bills, malformed eyes, extra limbs, etc.) were prevalent in common terns, Caspian terns, and black-crowned night herons on Lake Ontario (Gilbertson, 1975, Gilbertson et al. 1976). Currently on Green Bay, Wisconsin, Forster's terns, and double-crested cormorants are exhibiting a high incidence of deformities (Harris et al. 1985). The high prevalence, which is from 50 to 100x that of populations outside of the Great Lakes area, indicates an association with the high chemical burden of these species.

### 3.3.6 CAUSE-EFFECT RELATIONSHIPS IN FISH-EATING BIRDS

During the 1960s toxicologists continuously tested industrial chemicals such as PCBs in chickens, pigeons, and doves as well as by injecting eggs to observe what effects occurred. Pericardial edema in poultry (chick-edema or hydro-pericardium factor) had been linked to PCB mixtures contaminated with more toxic chlorinated dibenzofurans (Vos et al. 1970). Some chlorinated dibenzo-p-dioxins, specifically tetrachloro and hexachloro isomers (Firestone, 1973) and chlorinated azobenzenes (Shrankel et al. 1982) also induce chick edema. Symptoms of chick edema disease were present in Lake Ontario and Lake Erie herring gull colonies in 1974 (Gilbertson and Fox, 1977, Gilbertson, 1983). Other observations in gulls include high porphyrin levels, growth reduction, and enlarged livers. These observations are consistent with the known toxicological effects of one or more common Great Lakes contaminants originating from special waste including PCBs, chlorinated dioxins and hexachlorobenzene (HCB). HCB is a well-known porphyrogenic agent but is not chick-edema active. The prime suspect for much of the pathology and poor reproductive success in these birds is however 2,3,7,8 tetrachlorodioxin which is chick-edema active, and the most embryotoxic, teratogenic, hepatotoxic, and porphyrinogenic substance tested in chicken embryos (J.H. Koemen and J.J.T. Strik, personal communication)

The halogenated aromatic hydrocarbons such as PCBs, chlorinated dioxins and dibenzofurans that have been tested to cause chick-edema and porphyria are also strong inducers of liver enzymes such as aryl hydrocarbon hydroxylases. Levels of these liver enzymes were found to be elevated in herring gulls from Lake Ontario and Saginaw Bay and were directly correlated with the elevated levels of 2,3,7,8 tetrachlorodioxin found in embryos from those herring gull colonies (Ellenton et al, 1985).

### 3.3.7 RECENT POPULATION LEVEL EFFECTS IN HERRING GULLS

Trends in herring gull reproductive success from 1972 to 1981 are shown in Table 6. The data indicate that reproductive success improved rapidly from 1975 to 1977 in Lake Ontario and in eastern Lake Erie. This trend corresponds with the rapid declines of PCBs, DDT, mirex, photomirex, hexachlorobenzene and 2,3,7,8 tetrachlorodioxin residues present in gull eggs, fish and sediments in that area (see Chapter 2). An improvement in Lake Huron is also evident during the same time period although reproductive success was not severely impaired in colonies from that lake. Lake Superior colonies on the other hand have gone from normal reproductive success up to 1980 into a rapidly declining mode. Toxaphene was discovered in fish from Lake Superior and northern Lake Huron and Lake Michigan in 1982 and although this compound is present in all of the Great Lakes, the highest levels are found in Lake Superior. Therefore chemical agents such as toxaphene may be the cause of this recent failure.

## 3.4 CHRONIC EFFECTS OF PERSISTENT TOXIC CHEMICALS IN WILD MAMMALS

### 3.4.1 MINK

Mink live along the banks of lakes, marshes, creeks, rivers and the seashore. They occasionally enter cities by following

Table 6

**Average Number of Herring Gull Chicks (to 21 Days of Age) per Nest on the Main Monitor Colonies and Scotch Bonnet Island between 1974 and 1981**

| Location | 1972 | 1974 | 1975 | 1976 | 1977 | 1978 | 1979 | 1980 | 1981 |
|---|---|---|---|---|---|---|---|---|---|
| **Lake Ontario** | | | | | | | | | |
| Snake Island | 0.21 | | | | 1.01 | 0.86 | 1.60 | 1.49 | 1.73 |
| Sct Bonnet I | 0.12 | | 0.15 | | 1.10 | 1.01 | | | 2.13 |
| Mugg's Island | | | | | 1.52 | 1.47 | 1.56 | | 1.40 |
| **Lake Erie** | | | | | | | | | |
| Pt. Colborne Bkw | | 0.48 | 0.65 | 0.79 | | 1.45 | | | |
| Middle Island | | | | | | 1.70 | 1.63 | 1.62 | 2.10 |
| **Lake Huron** | | | | | | | | | |
| Chantry Island | | | 1.48 | | 1.12 | 1.40 | 2.17 | 2.17 | 2.16 |
| Double Island | | | | | | 1.57 | 2.17 | 2.25 | 2.23 |
| **Lake Superior** | | | | | | | | | |
| Agawa Rocks | | | | | | 1.66 | 0.88 | 0.40 | 0.37 |
| Granite Island | | | 1.32 | 1.55 | | 1.12 | 1.70 | 1.40 | 0.46 |

from Mineau *et al.* 1985.

waterways. The summer diet of mink consists primarily of crayfish, frogs and fish whereas the winter diet consists of other mammals such as muskrat mice and moles.

Reproduction of mink is extremely sensitive to organochlorine contaminants such as PCBs. Levels as low as 0.30 mg/kg (ppm) in the diet have impaired reproduction of commercially raised ranch mink (Platonow and Karstad, 1973) Survival of kits was severely reduced. DDT in combination with PCBs has also produced reproductive impairment in mink (Jensen et al., 1977). This phenomenon was first noticed in Michigan and Ontario ranch mink which could no longer reproduce when contaminated Great Lakes fish were added as a supplement to their diet. Reproductive impairment was not permanent and reproductive capacity returned when PCB-contaminated food was removed from the diet (Aulerich and Ringer, 1977).

Mink are also sensitive to uptake of mercury residues from their diet, initially showing uncoordination, loss of balance, followed by paralysis and death at dietary levels as low as 5 ug/kg (ppm).

Studies by the Canadian Wildlife Service (unpublished data) during 1979 showed that PCBs were detectable in all samples collected from southern Ontario and James Bay and that body burdens in Southern Ontario north of Lake Erie ranged consistently as high as 0.50 mg/kg to 1.25 mg/kg which was considered high enough to impair reproduction of mink in that area.

### 3.4.2 BELUGA WHALES

Recently, studies on the Beluga Whale population in the lower St. Lawrence River have shown that the population is severely depleted. Levels of PCBs as high as 575 mg/kg (ppm) have been found in whale blubber and 1725 mg/kg (ppm) in breast milk from the whales. Mirex has also been found in the river indicating the direct connection of the St. Lawrence River ecosystem with the Lake Ontario ecosystem and that Lake Ontario contaminants are affecting this sensitive species. Levels of organochlorine contaminants this high are considered to be producing severe chronic effects in the Beluga population (D.F.O. 1985).

## 3.5 CHRONIC EFFECTS OF PERSISTENT TOXIC CHEMICALS IN FISH POPULATIONS

One percent of the animal kingdom consists of mammals and birds. The other 99% consists of cold-blooded vertebrates such as reptiles, amphibians and fish and invertebrates such as oysters, clams, insects, lobsters, starfish, corals, sponges and worms.

By the end of the 19th century about 30 probable neoplasms of these lower animals had been described in the scientific literature. While most originated in fish, a few had also been found in reptiles, amphibians and bivalve mollusks.

Lower animals such as frogs and fish have led to the major discoveries regarding the cause of specific cancers. One discovery resulted from a worldwide outbreak of liver cancer in hatchery-raised rainbow trout which coincided with the introduction of plant based pelleted food. A mold growing on peanuts used in the trout food produced a toxin whose carcinogenicity was unknown at that time. Today, the aflatoxins produced by the mold, Aspergillus flavus, are recognized as extremely potent carcinogens that readily produce cancer in rodents and are epidemiologically linked to human liver cancer. This mold readily grows on improperly dried, stored grain as well as insect damaged grain in the field. Standards for aflatoxins in such food as peanut butter, resulting from this discovery in hatchery trout, have undoubtedly prevented many human cancers.

Current data show neoplasms in all classes of cold-blooded vertebrates and three phyla of invertebrates. Oncogenes, currently being investigated as the genetic basis for cancer, occur all the way down the phylogenetic tree to the sponges. Two hundred and eighty-seven species of fish are known to have neoplasms and, as in mammals, fish neoplasms originate from numerous cell types in all tissue systems with morphological and behavioral traits virtually identical to their mammalian counterparts (Harshbarger, 1983).

The terms "neoplasm" and "tumour" are synonyms for deviant populations of cells with a heritable abnormality which gives a degree of autonomy from host control. Minimally deviant, non-invasive neoplasms are benign. Moderately to highly deviant, invasive, destructive, possibly metastatic, eventually lethal masses are called cancer. However, regardless of what they are called, many benign neoplasms are a threat as they may progress on to cancer. While in some types of benign neoplasms this rarely if ever occurs or takes a very long time, many others demonstrate an insidious progression from benign to malignant. This appears to be the case for liver and skin neoplasms in fish.

Some fish tumours are caused by carcinogenic chemicals. At least 35 mammalian carcinogens have experimentally induced cancer in one or more of some dozen species of fish (Harshbarger, 1983). These chemicals produced liver cancer but cancer also occurred fairly often in the epidermis or skin, the epithelium of the digestive tract, and the kidney with occasional occurrence in the pancreas, gonad, air bladder, skeletal muscle and pigment cells. The cause of some types of fish neoplasms have not been determined. Others, such as the prevalent, widespread, malignant lymphoma of northern pike, are caused by viruses.

The liver is a prime target organ for carcinogenic chemicals. Fish, like mammals, utilize the cytochrome-mediated mixed function oxidases produced by liver microsomes to metabolize and eliminate a wide variety of chemical pollutants acquired with food or by contact. Many organic carcinogens are not themselves carcinogenic until metabolically activated by these liver enzymes. The actual carcinogenic intermediates are thought to be epoxides which bind to DNA (Hallett and Brecher, 1985). Neoplastic transformation possibly results from an ensuing de-regulation of oncogenes which then produce excess growth factors.

In a Canadian program initiated by the Department of Fisheries and Oceans, a major survey was conducted on several species of fish in a number of locations along the Canadian Great Lakes shoreline (Shear, 1985). The results of this survey, Table 7, indicated a high tumour frequency in white sucker which is widely distributed throughout the lakes. A pattern of increased frequency of sucker lip papillomas corresponded to areas of known industrial effluent discharges, particularly western Lake Ontario when the data was normalized for animal size (Figure 10).

More extensive studies have been carried out by U.S. researchers. Black (1983) has found epizootic brown bullhead liver and skin cancer in the Buffalo River adjacent to the Niagara River plus various types of neoplasms in six other species of fish. Extracts of Buffalo River sediments contained several dozen aromatic hydrocarbons including known carcinogens such as benzo(a)pyrene. Skin and liver cancer in brown bullheads were induced with these extracts. Thus, a circle of proof has been completed: fish were found with cancer, analyses of sediment extracts revealed suspected carcinogens and controlled laboratory exposures of fish to the extract induced the same types of neoplasms. The previous discovery of carbazoles also has possible significance for the Buffalo River location because dye industries bulldozed by-products into the river leaving

## Table 7

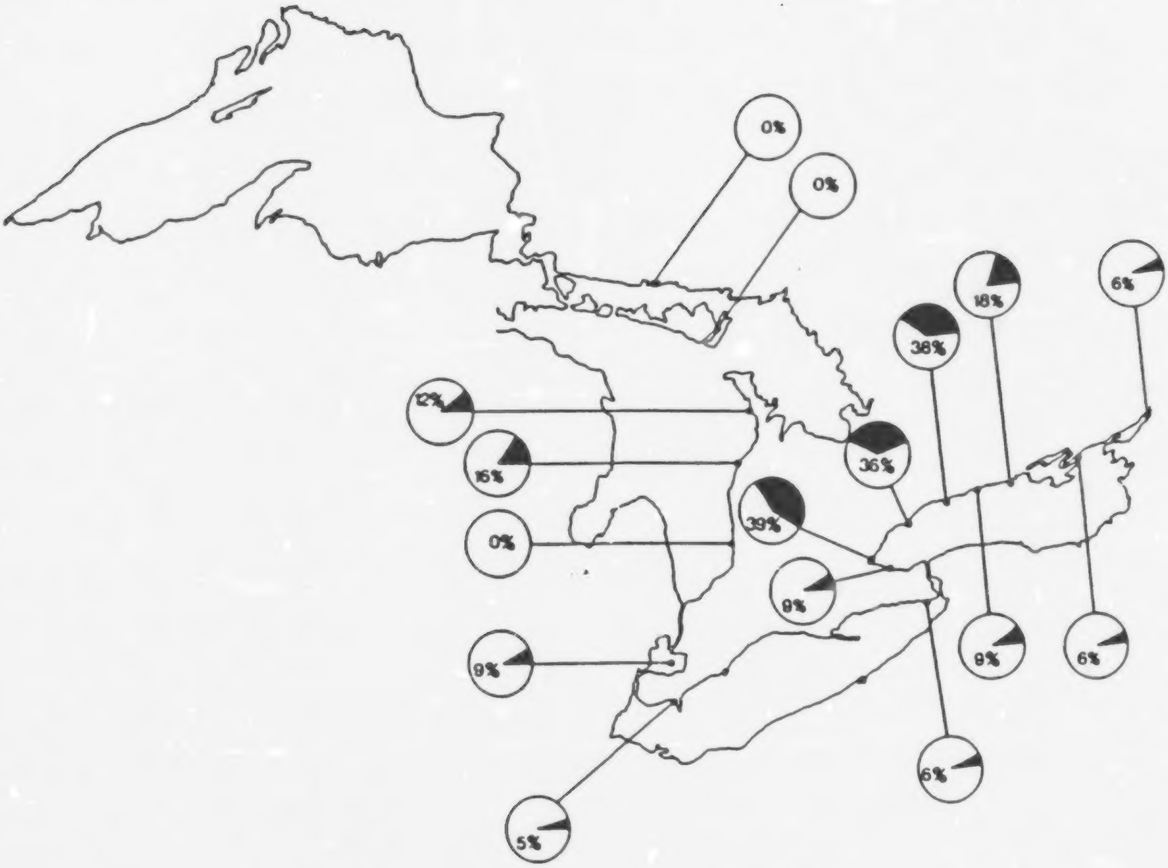
## Availability of Fish at Sampling Locations and the Frequency of Pathological Anomalies at These Sites

| Species | Pathological Condition | Number of Site Species Captured | Number of Sites Condition Recorded |
|---|---|---|---|
| Brown bullhead | Papilloma | 14 | 8 |
| Carp | Gonadal tumour | 12 | 3 |
| Carp X goldfish hybrid | Gonadal tumour | 6 | 6 |
| Channel catfish | Papilloma | 8 | 1 |
| Coho | Thyroid hyperplasia | 4 | 3 |
| Drum | Epidermal hyperplasia | 9 | 1 |
| Gizzard shad | Epidermal hyperplasia | 8 | 0 |
| Golden and silver redhorse | Papilloma | 9 | 2 |
| Longnose sucker | Papilloma | 2 | 1 |
| Pike | Lymphosarcoma | 9 | 0 |
| Walleye | Lymphocystis | 15 | 7 |
| White sucker | Papilloma | 23 | 17 |
| Yellow perch | Gonadal tumour | 16 | 8 |

Source: Shear, 1985

Figure 10

Prevalence (%) of epidermal papilloma on White Suckers


0%
0%
6%
18%
38%
12%
36%
16%
39%
0%
8%
9%
6%
9%
6%
5%

Source: Shear, 1985.

conspicuous multicolored dye traces in the river bank (Experimentally carbazobles produce liver cancer in rodents). Further work is needed to identify the specific carcinogen or group of carcinogens responsible and to determine if carbazole is present.

The Puget Sound and tributaries location has been extensively studied by Dr. Donald Malins and co-workers (1984). With their discovery of liver cancer in English sole in the Duwamish River estuary in 1975-76, the health of fish, crabs, shrimp, clams and worms was surveyed in clean and polluted sites throughout Puget Sound including Seattle, Tacoma and Everett, Washington. Sediment and animal tissues were analyzed for aromatic hydrocarbons, PCBs, chlorinated butadienes and metals. More than 500 aromatic hydrocarbons were found in just one sediment sample with 27 selected target compounds being up to 30 times higher in urban than reference areas. Epizootic, full-blown liver cancer in English sole and starry flounder from several sites reached 25% in English sole in the Duwamish River estuary. This percentage would be considerably higher if it included early tumours that had not progressed to full-blown cancers and if it eliminated fish below the age of first tumour development. A significant aspect of this study was cluster analyses of cancer prevalence related to the types of chemicals present. These analyses showed that the liver cancer is correlated with the presence of aromatic hydrocarbons and metals. Subsequent analysis revealed carcinogenic dye intermediates, known as carbazoles. The presence of carbazoles had a highly significant correlation with English sole liver cancer (Malins et al, 1984).

Black and Baumann (personal communication) have done the same crucial experiment on sediment from the Black River, Ohio. Tumourous fish and contaminated sediment were taken from the vicinity of an outfall of a coking plant about 3 kilometres from where the river enters Lake Erie. In addition to inducing brown bullhead neoplasms, rodent skin cancers were also induced with Black River sediment extracts. Baumann and associates found that brown bullheads in the Black River had a 30% prevalence of grossly detectable cancers. If one adds cancerous and pre-cancerous lesions that can be found by microscopically examining liver tissue sectioned at seven levels, the prevalence of liver neoplasms in three-year-old and above Black River brown bullheads approaches 100%. Fishing is now prohibited in this area of the Black River. The river channel from the coking plant to Lake Erie is regularly dredged to permit the entry of ore ships and the dredge spoils are pumped into a landfill in Lake Erie.

The Hudson River is heavily contaminated, particularly with PCBs near Albany, where a large section of the river bed has been designated for cleanup under U.S. Superfund legislation. Tomcod fish in the Hudson River have the biggest and worst looking liver cancers of fish at any of the other locations (Harshbarger, 1985). Neoplasms range from foci of basophilic hepatocellular alteration to enormous masses of greatly enlarged, poorly-differentiated, neoplastic hepatocytes that frequently contain blood-filled lakes. Tomcod, which migrate out of the river into shallow bay water in fall and winter, were collected in the spring on their spawning run up river. Only 5% of the spawning run consists of two-year-old fish versus about 25% for other streams and virtually 100% of these two-year-olds have liver cancer.

Metals such as nickel, cadmium and arsenic in mine tailings have been suspected to be responsible for the liver cancer in sauger taken from Torch Lake, Michigan. The sauger population had extensive non-neoplastic visceral granulomas as well as several types of neoplasms in 1973. Sauger also had 100% liver cancers and that liver cancer was prevalent in Torch Lake walleyes (Black, 1982). Twenty percent of the lake was filled in with copper mine tailings.

## 3.6 DISCUSSION

Serious, population-level, toxic chemical-induced reproductive effects have been demonstrated historically in many fish-eating bird species in the Ontario environment. In certain locations reproductive failure is still occuring. Congenital anomalies, abnormal behavioural, and many other effects have also been observed, some of which are continuing. Multiple effects in these avian species are caused by multiple chemicals. The toxic chemicals of concern are chemicals which bioaccumulate up food chains. They are large molecules which are chlorinated and primarily originate as constituents of special waste.

The agricultural usage of DDT compounds and other chlorinated insecticides has been severely restricted for 16 years. Residue levels and effects due to agricultural usage of chlorinated insecticides have decreased dramatically since the restrictions.

Compounds such as mirex which originate from industrial discharges to two tributaries of Lake Ontario and toxaphene, a pesticide which originates in the southeastern U.S., have travelled great distances from their points of origin by water and air respectively.

Tumours in fish have been demonstrated in all areas studied so far with the frequency increasing dramatically up to 100% in highly polluted areas such as those near the coking operations on the Buffalo River and the Black River. Chemicals causing fish tumours include polyaromatic hydrocarbons, carbazoles (from dyes), and metals such as copper, cadmium, zinc, and arsenic. All of these chemicals are constituents of special waste.

The effects demonstrated in Ontario wild animals would be unacceptable if they were ever demonstrated in human populations.

Unfortunately epidemiological evidence is difficult if not impossible to obtain, since humans are more difficult to observe and study. The possibility of experimenting to demonstrate cause-effect relationships with humans as has been done with both birds, wild mammals and fish is not an option. For this reason, the only scientific option is to heed the warning from these studies of wild populations.

## 3.7 MAJOR FINDINGS

1. Impact of the Major Toxic Chemicals Originating from Special Waste in Ontario.

a) Population level effects, such as reproductive failure, increased incidence of congenital anomalies and abnormal behaviour in wild omnivorous or carnivorous birds of Ontario, reproductive failures of mammals such as mink, and increased incidence of fish tumours have been scientifically documented since the 1960s.

b) Although the widespread gross population effects such as the almost total reproductive failure of herring gulls, cormorants and herons in Lake Ontario stopped in 1977, other more subtle effects such as liver enzyme disfunction, and elevated incidence of fish tumours still occur in localized areas of the Great Lakes. Ontario mink cannot be fed Great Lakes fish as a source of protein, and herring gulls from certain areas such as eastern Lake Superior still exhibit reproductive failures.

c) Cause-effect relationships at the population level are evident for polynuclear aromatic hydrocarbons and certain fish tumour problems, and between chlorinated hydrocarbons such as PCBs, chlorobenzenes, chlorinated dioxins, and dibenzofurans and certain chlorinated pesticide residues and the reproductive problems found in Great Lakes herring gulls.

d) The Beluga whale population in the St. Lawrence River is currently suffering from reproductive impairment probably caused by the same toxic chemicals found in Lake Ontario.

e) Population-level effects in wild species represent serious problems from toxic chemical exposure since documented cause-effect relationships show long lag phases of more than 10 years duration between the chemical exposure and the population damage and between the decline of exposure and the improvement within the population. Therefore population-level effects in wild species (caused by toxic chemicals) represent serious problems since the effect may last for over 10 years after the cause has been removed.

f) The effects demonstrated in wild Ontario populations represent irreversible or terminal damage to the individuals within each species studied. These effects, such as total reproductive failure, would be considered totally unacceptable if they were demonstrated in human populations in Ontario especially if cause-effect relationships could be established.

# CHAPTER 4

# ECOSYSTEM PATHWAYS AND HUMAN EXPOSURE ROUTES TO SPECIAL WASTE

## 4.1 INTRODUCTION

Just as wild populations are exposed to toxic chemicals derived from special waste (Chapters 2 and 3), human populations are exposed to the same chemicals but through different pathways.

The multiple subtle chronic effects which manifest themselves in disease including terminal illnesses such as cancer, liver sclerosis, behavioural and neural disorders and diseases caused as a result of immunosuppression are very difficult to discern in human populations with statistical rigour.

In order to find the direct cause of these diseases one must determine both the nature of all the chronic effects or stresses which together caused the disease and also determine all of the most probable variables including toxic chemicals which may have caused the multiples of chronic effects. This investigation cannot generally be carried out until the disease is obvious at a population level. Because of the lag phase between cause and population effect (Chapter 3.2) the cause of the disease may have declined or may have been totally eliminated. Therefore it is important to understand human exposure to toxic chemicals, derived from special waste, which have the potential to produce human disease in the future or which may contribute to human disease currently. Knowledge of cancer and most other chronic illnesses is based on studies of the chronic effects which cause such diseases; laboratory experiments on animals or other predictive organisms which prove the cause-effect relationship between exposure to a toxic chemical and the chronic effect; and more expensive multi-year studies of the disease itself. Direct human studies have been impossible except for tragic accidental exposures or isolated occupational problems. Chapter 3 has shown that wild populations of animals have exhibited and are exhibiting the same chronic effects on a population wide level from environmental exposure to toxic chemicals derived from special waste as those which are exhibited in laboratory studies.

This forms the basis of scientific concern for long term human exposure to toxic chemicals. Industrial society as a whole has begun to take measures to prevent exposure to toxic substances. By reducing long-term exposure to toxic chemicals derived from special waste, disease manifested from the chronic effects caused by these chemicals will be prevented. This is especially true for those Ontario populations which may be predisposed to disease caused by chronic effects from toxic chemical exposure or those individuals who by habit or occupation may already be exposed or dosed at higher than average rates.

Prevention rather than reaction is the best scientific approach to the problem since reaction is always too late.

Prevention of human exposure to toxic chemicals derived from special waste requires an understanding of which toxic chemicals humans are exposed to, the basis of human exposure, the environmental pathways which cause this exposure, and finally what critical populations of Ontario citizens might be exposed to relatively high levels of these chemicals. From this analysis one can then begin to understand the sources and types of special waste which must be mitigated by better waste management.

## 4.2 TOXIC CHEMICAL RESIDUES IN ONTARIO RESIDENTS

This section documents the current knowledge of residue levels in the Ontario Population.

Herring gulls and the coho salmon living in Lake Ontario have a common food source, ie. alewives and smelt which are the next step lower on the food chain. Alewives and smelt are the common source of PCBs, DDE, mirex, photomirex, and chlorobenzenes to the gulls and salmon (Table 8) (Norstrom et al., 1978). The same relationship for 2,3,7,8 TCDD can be shown (NRC, 1982).

The human population in Ontario contains residues similar to those found in Lake Ontario herring gulls and fish (Table 8). This finding demonstrates that humans are exposed to the same environmental contaminants derived from special waste as fish and wildlife.

## TABLE 8
## Human Residues in Ontario

| | Adipose Tissue (mg/kg) | | Breast Milk -fat basis (mg/kg) | |
|---|---|---|---|---|
| | Kingston (1) | Ottawa (1) | Ontario (2) | Ontario (2) |
| PCB | 3.0 | 2.0 | 2.1 | 0.76 |
| DDT | 3.429 | 2.694 | 2.6 | 0.73 |
| Mirex | 0.027 | 0.011 | <0.005 | - |
| Photomirex | 0.009 | 0.006 | - | - |
| HCB | 0.106 | 0.078 | 0.017 | 0.009 |
| BHCH | 0.136 | 0.065 | 0.006 | <0.005 |
| 2,3,7,8 -TCDD (4) | $12.4 \times 10^{-6}$ | $8.6 \times 10^{-6}$ | - | - |
| Heptachlor epoxide | 0.035 | 0.037 | 0.083 | <0.005 |
| Dieldrin | 0.036 | 0.043 | 0.029 | <0.005 |
| | n=12 | n=10 | n>47 | n>125 |

### Wildlife and Fish Residues in Ontario[3]

| | Alewives and Smelt (mg/kg) | Coho Salmon (mg/kg) | Herring Gull eggs (mg/kg) |
|---|---|---|---|
| PCB | 2.21 | 5.7 | 138 |
| DDE | .47 | .97 | 17.4 |
| Mirex | .09 | .23 | 4.4 |
| Photomirex | .03 | .11 | 1.6 |
| HCB | .024 | .097 | 0.52 |
| BHCH | .002 | .012 | .078 |
| TCDD (5) | $14 \times 10^{-6}$ | $30 \times 10^{-6}$ | $55 \times 10^{-6}$ |
| Heptachlor epoxide | .003 | .015 | .007 |
| Dieldrin | .029 | .087 | .060 |

Sources:
1 = Williams et al., 1984
2 = Frank, R., (personal communication)
3 = Norstrom et al., 1978
4 = Ryan et al. 1983
5 = NRC 1982

Frank et al., 1983 collected data on PCB residues in human adipose tissues from 1976 to 1981 (Figure 11). The data do not show significant differences in residue levels between sexes. The sample size used is insufficient to draw any conclusions on trends. Many residues are prevalent in adipose tissue from humans across Canada as shown in Table 9 (Mes et al., 1982).

### 4.2.1 PCBS IN BREAST MILK

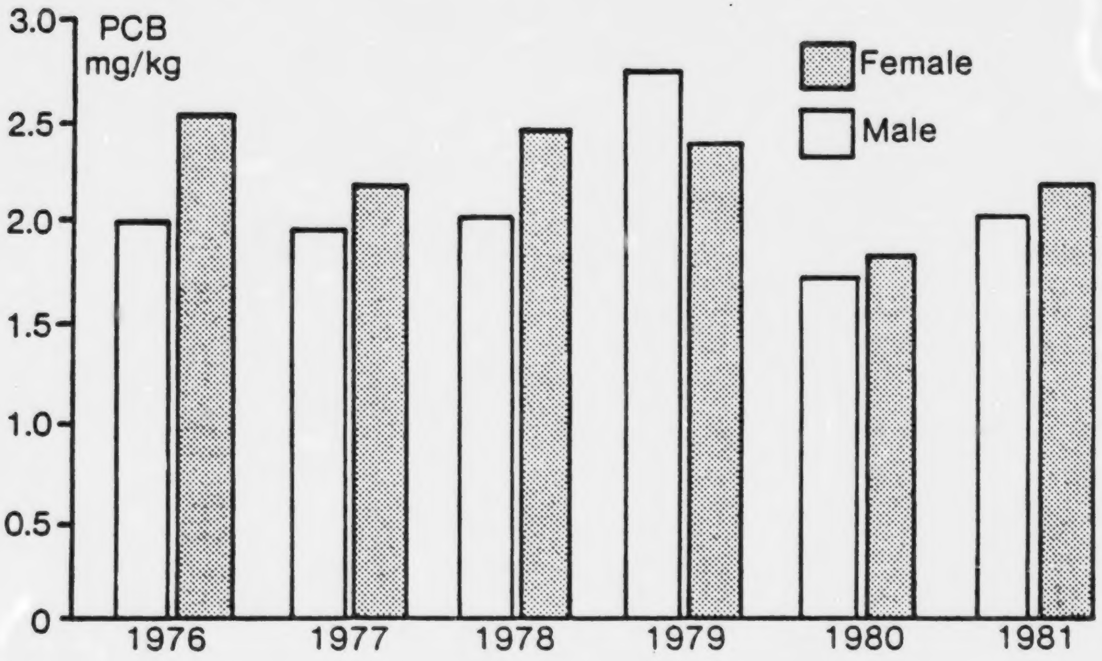
In a study of mothers' milk in Sheboygan Wisconsin, women who consumed fish at least twice a month had a PCB content in their breastmilk of 1.26 mg/kg milkfat compared to the breastmilk PCB content of those who ate no fish of 1.07 mg/kg (Smith, 1984). The mothers' mean PCB blood serum levels were 0.6 ug/kg for fish-eaters and 0.5 ug/kg for non fish-eaters in the study.

A study of Great Lakes fish-eaters showed a significant difference between serum PCB levels of lake trout eaters compared with controls (Humphrey, 1983). This exposed group consumed greater than 10.91 kg/a of fish that ranged from 0.4 to 5.4 mg/kg in PCB content. Serum residue levels from nursing mothers who were not fish-eaters ranged from 10 to 23 parts per billion whereas residue levels in serum from fish-eating mothers ranged from 41 to 105 parts per billion.

PCBs have been reported in human milk (Ritcey et al., 1972; Musial et al., 1974; Mes and Davies, 1979; Frank et al., 1983). A nation-wide survey by Mes and Davies (1979) of PCBs in the milk

**Figure 11**

PCB Concentration in Human
Adipose Tissue Ontario 1976-81



Source: Frank, R., et. al., 1983a.

## Table 9

## Residues in Human Fat

| Compound | Amount (ug/kg wet weight) | Percentage of samples containing residues |
|---|---|---|
| PCB | 907 | 100 |
| Hexachlorobenzene | 62 | 100 |
| BHC (lindane) | 65 | 88 |
| Oxychlordane | 55 | 97 |
| Trans-nonachlor | 65 | 99 |
| Heptachlor epoxide | 43 | 100 |
| Dieldrin | 69 | 100 |
| p,p'-DDE | 2095 | 100 |
| o,p'-DDT | 31 | 63 |
| p,p'-TDE | 6 | 26 |
| p,p'-DDT | 439 | 100 |

* Values are means.

Source: Mes et al., 1982.

of Canadian mothers indicated that the highest average PCB levels were found in Ontario and Western Canada (Figure 12). Frank et al. (1983) analyzed samples of milk and human adipose tissue from Ontario residents and found no apparent differences in organochlorine residues between rural and urban populations. They also found no significant differences in human milk samples from year to year. (Table 10) (Frank et al., 1985.) In Ontario, mothers' milk was found to contain 0.583 mg/kg PCBs on a milkfat basis, almost 25 times the levels in Ontario cows' milk. Other persistent residues are prevalent in mothers' milk (Table 8) which parallel the residue patterns found in human body fat.

## 4.3 HUMAN EXPOSURE ROUTES

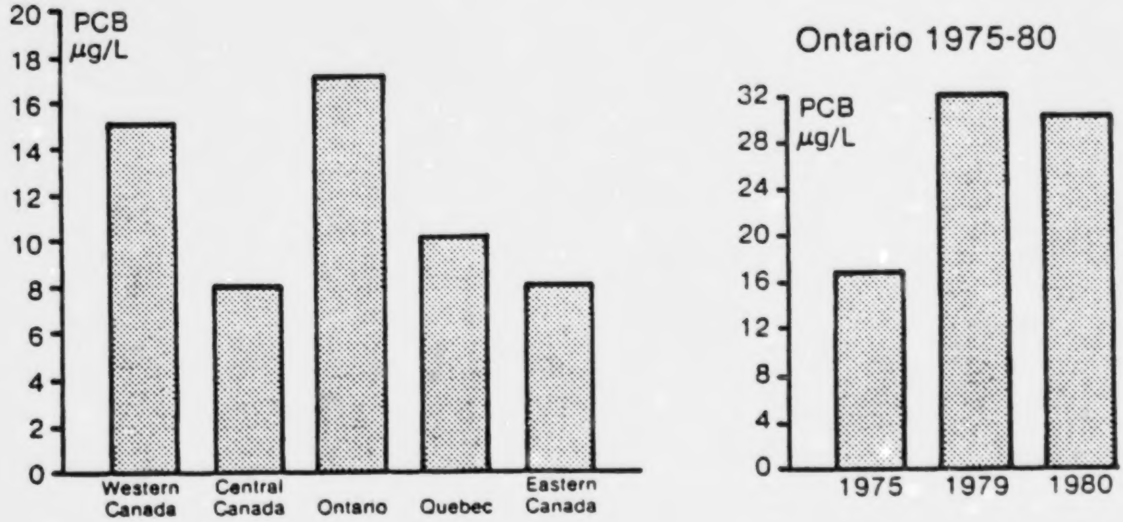
Since herring gulls and coho salmon accumulate these residues from their common food supply it seems logical to consider the human exposure routes thoroughly, particularly the food supply.

### 4.3.1 HUMAN EXPOSURE MODELS FOR PCBS AND 2,3,7,8 TCDD

A study by Bennet (1983) followed total non-occupational environmental exposure of PCBs to humans. This study revealed that for PCBs the atmospheric pathway contaminates plants directly, livestock indirectly and that the diet ultimately contributes the major human environmental dosage of PCBs (Figure 13). Exposure from drinking water and the atmosphere directly are inconsequential relative to food exposure. A more recent

Figure 12

Arochlor 1260 in Mother's
Milk 1975 Canada Wide



Source: Mes, J. and Davies, D.J., 1979.

## Table 10

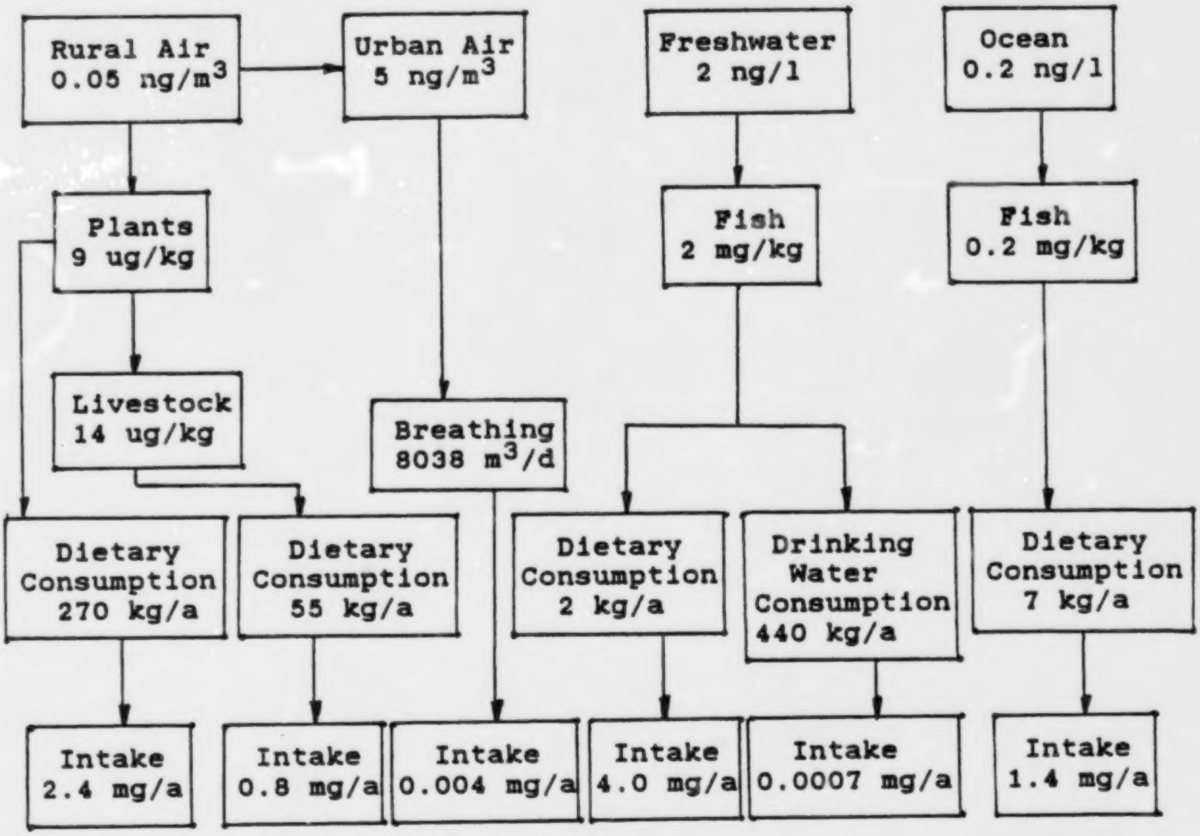
### Mean Concentrations and Estimated Exposure to PCBs in Human Milk Samples from Ontario Residents 1971 - 1985

| | Concentration | |
|---|---|---|
| Year | Mean (mg/kg fat) | Mean (mg/kg whole milk) |
| 1971-72 | 1.20 | 0.036 |
| 1973-74 | 1.18 | 0.035 |
| 1977 | 0.80 | 0.024 |
| 1978 | 0.066 | 0.002 |
| 1979 | 0.96 | 0.028 |
| 1981 | 0.79 | 0.024 |
| 1983 | 1.24 | 0.037 |
| 1985 | 0.67 | 0.020 |

Source: Frank, 1986

Figure 13

Human Exposure Pathways to Background Environmental PCBs


Rural Air 0.05 ng/m3
Urban Air 5 ng/m3
Freshwater 2 ng/l
Ocean 0.2 ng/l
Plants 9 ug/kg
Fish 2 mg/kg
Fish 0.2 mg/kg
Livestock 14 ug/kg
Breathing 8038 m3/d
Dietary Consumption 270 kg/a
Dietary Consumption 55 kg/a
Dietary Consumption 2 kg/a
Drinking Water Consumption 440 kg/a
Dietary Consumption 7 kg/a
Intake 2.4 mg/a
Intake 0.8 mg/a
Intake 0.004 mg/a
Intake 4.0 mg/a
Intake 0.0007 mg/a
Intake 1.4 mg/a

Source: Bennet, 1983.

modelling effort (MacKay et al., 1985) shows that 2,3,7,8 TCDD is transmitted from air to soil and then to plants and livestock resulting in food again being the major route of exposure (Figure 14).

### 4.3.2 HUMAN EXPOSURE TO PERSISTENT TOXIC CHEMICALS IN FOOD

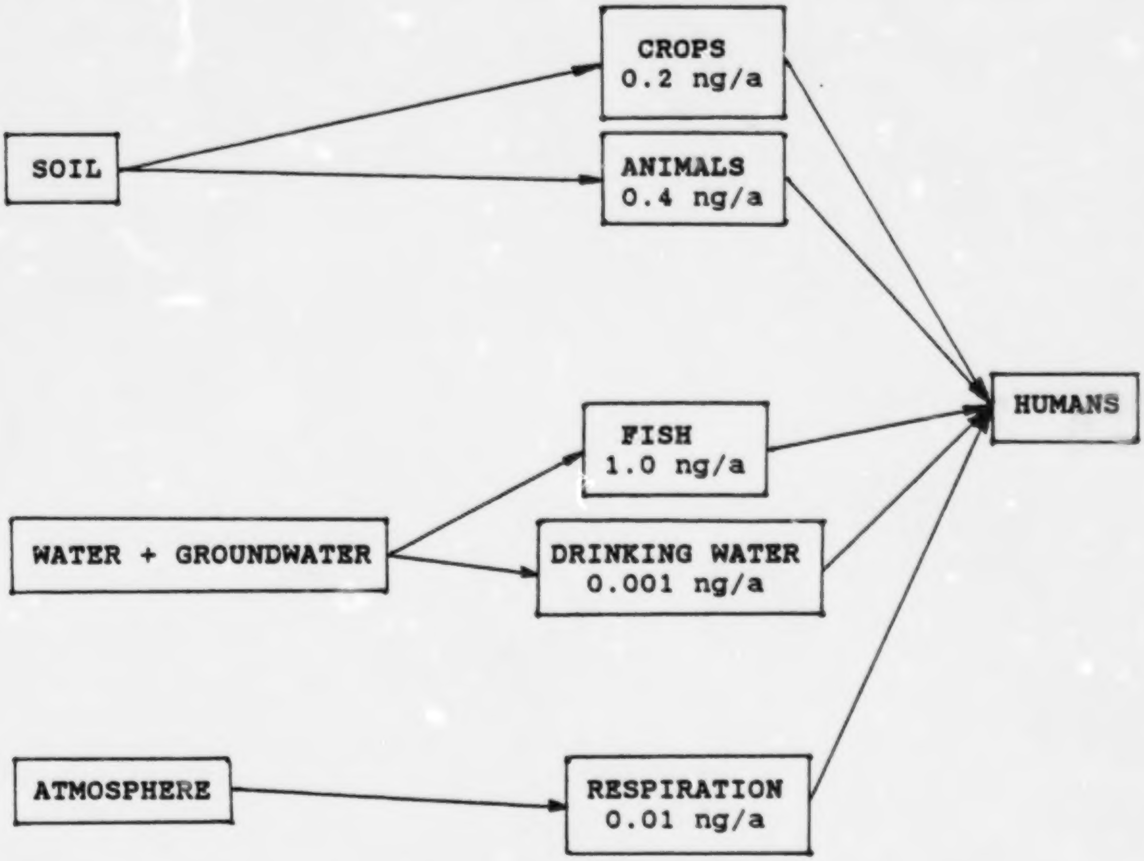
Foods have been analysed individually and in composites for the presence of persistent toxic chemicals in the U.S. Since 1964, the U.S. Food and Drug Administration has reported concentrations of pesticides, herbicides, fungicides and selected industrial chemicals in foods. Market basket studies have concentrated on the typical diet of the young adult male, representative adult diets, and separate evaluations of infant and toddler diets (Podrebarac, 1984; Gartrell et al., 1986).

Total diet studies have also been conducted in Canada (Smith, 1971; Smith et al., 1972; Smith et al., 1973; Smith et al., 1975; McLeod et al., 1980). McLeod et al., (1980) obtained data on the concentrations of pesticide residues in winter and summer food composites for five urban areas in Canada. Data for Toronto, Ontario, are shown in Table 11. PCB concentrations in food composites from 1980 - 1982 have also been determined by the Department of National Health and Welfare (Table 12) (Grant, 1985).

The trace metal content of a "representative" Canadian diet in 1972 was determined by Kirkpatrick and Coffin (1977). This study used foods obtained quarterly from the Winnipeg area. The

## Figure 14

Model of Annual Human Exposure to 2,3,7,8 TCDD


SOIL
CROPS
0.2 ng/a
ANIMALS
0.4 ng/a
WATER + GROUNDWATER
FISH
1.0 ng/a
DRINKING WATER
0.001 ng/a
ATMOSPHERE
RESPIRATION
0.01 ng/a
HUMANS

Source: Mackay et al., 1985.

## Table 11

## Selected Concentrations of Persistent Toxic Chemicals in Food Composites from Toronto (1976-1978)

| Food Group/ Chemical | Winter (mg/kg) | Summer (mg/kg) |
|---|---|---|
| **Cereals** | | |
| HCH | 0.2 | 2 |
| DDT | ND | ND |
| Diazinon | 3 | ND |
| **Meats** | | |
| HCH | 0.2 | 2 |
| DDT | 4 | 10 |
| Dieldrin | 1 | 1 |
| HCB | ND | 0.2 |
| PCBs | ND | 10 |
| **Potatoes** | | |
| DDT | 1 | ND |
| Dieldrin | 1 | ND |
| Endrin | ND | ND |
| HCB | ND | ND |
| **Fruits** | | |
| DDT | 4 | ND |
| Endosulfan | ND | ND |

Note:
ND = Not detected

Source: (McLeod et al., 1980)

## Table 12

## Average Concentrations of PCBs in Different Food Types in Canada (1980 - 1982)

| Food type | Average (mg/kg) |
|---|---|
| Fruit and fruit juice | <0.05 |
| Marine products | 0.47 |
| Pasta, cereals and bakery products | <0.05 |
| Beef fat | 0.063 |
| Pork fat | 0.049 |
| Pork - other | 0.471 |
| Poultry fat | 0.033 |
| Poultry - other | <0.05 |
| Oil, margarine, lard | 0.266 |
| Milk | 0.044 |
| Cheese | 0.010 |
| Eggs | 0.019 |

Source: Grant, 1985

results showed a relatively even distribution of cadmium throughout the diet of between 0.02 and 0.05 mg/kg. The meat composite was the only food type to contain a significant amount of mercury (0.029 mg/kg). The calculated average daily intake of the ten trace metals from food sources analysed in 1972 is shown in Table 13.

### 4.3.3 DAIRY PRODUCTS

Most of the research on residues of persistent toxic chemicals in dairy products has focused on cows' milk. Concentrations of persistent toxic chemicals in cows' milk in Ontario have been studied by Frank et al. (Frank et al., 1970; Frank et al., 1979; Frank et al., 1983; Frank, 1986). Dieldrin, DDE, hepta-chlor, heptachlor epoxide and alpha HCH all of which are organochlorine pesticides were found in over 90% of the samples. PCBs, lindane and pentachlorophenol (PCP) were found in 83, 68, and 57% of samples respectively. Four samples exceeded the permissible PCB concentration and one sample exceeded the permissible pentachlorophenol concentration. Residues of chlordane, endosulfan, TDE and DDT were identified in only 1.9 to 4.7% of the samples and were present at concentrations only slightly above the minimum detection level. Hexachlorobenzene (HCB) was identified at low concentration in 40% of the samples. The average concentrations of organo-chlorines are shown in Table 14.

## Table 13

## Estimated Total Daily Intake of Trace Metals from Canadian Food - 1972

| Metal | Daily Intake (ug/d) |
|---|---|
| Cadmium | 52 |
| Chromium | 284 |
| Cobalt | 36 |
| Copper | 1606 |
| Iron | 17398 |
| Lead | 77 |
| Manganese | 2930 |
| Mercury | 10 |
| Nickel | 409 |
| Zinc | 15550 |

Source: Kirkpatrick and Coffin, 1977

Residues of endrin, methoxychlor and mirex were not detected, neither were residues of six organophosphorus insecticides (ronnel, fenthion, trichlorfon, crufomate, crotoxyphos and coumaphos).

### 4.3.4 MEAT AND EGGS

Residues of organochlorine pesticides have been determined in fat from beef and pork carcasses marketed in Ontario between 1969 and 1981 (Table 15) (Frank et al., 1983). Another study examined ambient concentrations of organochlorines in beef, mutton, chicken and pork fat in Canada between 1969 and 1974 (Saschenbrecker, 1976). Concentrations of DDT decreased in all samples between 1969 and 1974, except chicken, but concentrations of PCBs increased over the same time period. Concentrations of organochlorines, including PCBs, in Ontario samples of beef and pork fat were much higher in this study than in the 1981 study discussed above.

Organochlorine residues have also been investigated in chicken and egg fat (Frank et al., 1985). This study reported concentrations between 1969 - 1982 in samples from Ontario. During this time total DDT and PCB residues decreased significantly in samples of chicken and egg fat. Dieldrin concentrations decreased less markedly. Chlordane and heptachlor epoxide were rarely detected (minimum detection level = 1 ug/kg);

## Table 14

## Average Concentrations of Organochlorine Residues in Cows' Milk in Ontario - 1983

| Chemical | Average Concentration (ug/kg butterfat) | Average Concentration (ug/kg whole milk) |
|---|---|---|
| Total DDT | 12 | 0.46 |
| A-HCH | 6.2 | 0.24 |
| G-HCH | 4.8 | 0.18 |
| Heptachlor epoxide | 3.4 | 0.13 |
| Dieldrin | 6.2 | 0.24 |
| HCB | 0.67 | 0.02 |
| Total PCBs | 24 | 0.91 |
| PCP | 29 | 1.10 |

Note:
A = alpha
G = gamma

Source: Frank et al., 1985b

## Table 15

## Summary of Average Concentrations and Estimated Human Exposure to Organochlorines in Beef and Pork Fat from Ontario (1981)

| Chemical | Beef<br>Mean Concentration (ug/kg fat) | Pork<br>Mean Concentration (ug/kg fat) |
|---|---|---|
| Total DDT | 12 | 5 |
| Dieldrin | 5.7 | <1 |
| Heptachlor epoxide | 4.2 | <1 |
| Chlordane | 1.1 | <1 |
| A-HCH | 6.6 | 1.1 |
| G-HCH | 2.9 | 13 |
| PCB | 9.5 | 3 |

Note:
A = alpha
G = gamma

Source: Frank et al. 1983b

however, the incidence in chicken fat increased after 1973. This was probably a result of the removal of aldrin, dieldrin and heptachlor in 1969 from use for soil insect control, and the subsequent increased use of chlordane until 1977. Lindane residues were infrequently detected. A summary of the most recent data (1981 - 82) is shown in Table 16.

In contrast to these data, a 1982 study of 203 Canadian chicken eggs reported a mean PCB concentration of 0.0008 mg/kg, with a maximum concentration of 0.006 mg/kg, (Canviro Consultants, 1985).

Recent Canadian data on residues of organochlorines in different types of meat have been released by Agriculture Canada. The report describes concentrations in samples taken between March 1984 and March 1985 (Agriculture Canada, 1985) and includes data on other human and animal foodstuffs for many different pesticides. Residues derived from special waste were not studied. Selected data from this report are shown in Table 17.

Polychlorinated dibenzo-p-dioxins have also been identified in several types of meat. Livers of Ontario chickens raised on wood shaving litter containing pentachlorophenol have been shown to contain PCDDs. Concentrations ranged from not detected (ND) to 1.42 ug/kg for H6CDD, ND to 0.57 ug/kg for H7CDD and ND to 0.66 ug/kg for O8CDD Octachlorodibenzofuran was also detected at ND to 0.13 ng/g. Pentachlorophenol was also associated with PCDD

## Table 16

### Summary of Organochlorine Residues in Chicken and Egg fat (1981 -1982)

| Chemical | Chicken<br>Mean Concentration[1] (ug/kg fat) | Eggs<br>Mean Concentration[1] (ug/kg fat) |
|---|---|---|
| Total DDT | 2.3 | 3.9 |
| Dieldrin | 0.74 | ND |
| Heptachlor epoxide | 4.6 | ND |
| Chlordane | 4.6 | ND |
| G-HCH | 0.4 | ND |
| PCB | 4.8 | ND |

Note:
G = gamma

Source: Frank et al., 1985b

## Table 17
## Concentrations of Organochlorine Pesticides in Beef, Chicken and Pork (1984 - 1985)

| Chemical | Range (mg/kg) | Mean (mg/kg) |
|---|---|---|
| | **BEEF** Concentrations[1] | |
| Aldrin/ Dieldrin | 0 - 0.050 | 0.001 |
| A, B-HCH | 0 - 0.034 | 0.003 |
| Chlordane | 0 - 0.120 | 0.001 |
| DDT | 0 - 0.0330 | 0.006 |
| Endosulfan | 0 - 0.042 | 0.001 |
| Endrin | ND | ----- |
| Heptachlor | 0 - 0.022 | 0.001 |
| HCB | 0 - 0.026 | 0.001 |
| G-HCH | 0 - 0.150 | 0.002 |
| Methoxychlor | ND | ----- |
| Toxaphene | ND | ----- |
| | **CHICKEN** | |
| Aldrin/ Dieldrin | 0 - 0.039 | 0.001 |
| A, B-HCH | ND | ----- |
| Chlordane | ND | ----- |
| DDT | 0 - 0.017 | 0.001 |
| Endosulfan | ND | ----- |
| Endrin | ND | ----- |
| Heptachlor | ND | ----- |
| HCB | ND | ----- |
| G-HCH | 0 - 0.100 | 0.002 |
| Methoxychlor | ND | ----- |
| Toxaphene | ND | ----- |
| | **PORK** | |
| Aldrin/ Dieldrin | ND | ----- |
| A, B-HCH | ND | ----- |
| Chlordane | 0 - 1.640 | 0.007 |
| DDT | 0 - 0.328 | 0.002 |
| Endosulfan | ND | ----- |
| Endrin | ND | ----- |
| Heptachlor | 0 - 0.020 | 0.001 |
| HCB | ND | ----- |
| G-HCH | 0 - 0.193 | 0.002 |
| Methoxychlor | ND | ----- |
| Toxaphene | ND | ----- |

Note:
DDT includes DDD and DDE
Endosulfan includes aplha and beta isomers and endosulfan sulphat
Heptachlor includes heptachlor epoxide

Source: Agriculture Canada, 1985

contamination of young Ontario pigs: skin, liver, kidney and brain tissues were found to contain 32 - 70 pg/g of H6CDD, 790 - 1670 pg/g of H7CDD and 27 - 4800 pg/g of O8CDD (Ryan, 1983). All of these residues were found on sick or dead animals.

A recent provincial report (MOE, 1985a) discussed PCDD and PCDF concentrations in Canadian meat and eggs.

a) Poultry - 12% of samples of Canadian chicken fat taken in 1980 contained PCDD and PCDFs at detectable levels up to 0.4 ug/kg. There were mainly H6-, H7- and O8CDD, with O8CDD comprising about 60% of the total residues. No T4- and P5-CDDS or CDFs were found and O8CDF was not detected.
b) Pork - samples of Canadian pork fat can contain up to 0.5 ug/kg of PCDDs, mainly H7- and O8CDD. O8CDD can constitute up to 85% of the total residue found.
c) Beef - 10% of North American abattoir samples contained H6-, H7- and O8CDD in the low ug/kg range.
d) Eggs - Canadian eggs can contain up to 0.1 ug/kg of O8CDD.

In order to obtain exposure information on PCDDs and PCDFs as well as current information on PCBs and other persistent residues, a direct food composite survey was taken from supermarkets throughout the city of Toronto in the summer of 1985. (Davies, 1986a). Only food grown in Ontario was sampled. Food was divided up into five categories: leafy vegetables, root vegetables, fruit, milk, and meat and eggs. Chlorobenzenes were detected in all composites with the most common congeners being the trichloroisomers. Lindane was detected in all composites except cows' milk. Other hexachlorocyclohexane isomers were also prevalent. DDT and its metabolites were still found in all composites. PCBs were detected in fruit, milk, and meat/egg composites with the highest concentration found in fruit. Concentrations of all the above residues when detected ranged from 0.1 to 1 ug/kg on a fresh weight basis.

Residues of PCDDs and PCDFs were detected in highest concentration in the fruit composite with the predominant residues being P5CDF, (0.28 ug/kg), H6CDF (2.0 ug/kg), H6CDD (0.45 ug/kg), H7CDF (6.6 ug/kg), H7CDD (1.2 ug/kg) O8CDF (1.2 ug/kg) and O8CDD (1.2 ug/kg). Residues in milk were the second highest with the predominant congeners being T4CDF, T4CDD, P5CDF, H7CDF, H7CDD, O8CDF, and O8CDD all found between 0.01 and 0.1 ug/kg. Root vegetables and the meat/egg composite were contaminated at lower concentrations. These residue concentrations fit well with the fugacity III model prediction of Mackay et al (1985a) and begin to show that our food is the major exposure route for PCDDs and PCDFs.

## 4.3.5 HUMAN EXPOSURE TO PERSISTENT TOXIC CHEMICALS IN DRINKING WATER

Persistent toxic organic chemicals are soluble in water at relatively low concentrations. Toronto's drinking water is the largest supply system on Lake Ontario. Water samples have been analysed for the presence of 135 organic and 35 inorganic chemicals. Between 1978 and 1984, 51 chemicals were identified although most were detected infrequently at concentrations well below the provincial drinking water objectives. A recent study estimated the average concentrations of chemicals detected between 1978 and 1984 (Davies, 1986b). Assuming an average consumption of two litres a day (Dept. of National Health and Welfare, 1978) human exposure estimates were calculated from these average concentrations. The average concentrations and the estimated human exposures are shown in Table 18. No PCBs, lead or heptachlor have been detected in Toronto's drinking water.

Drinking water quality in the Niagara area and Lake Ontario (MOE, 1984a) is shown in Table 19. This study also analysed water samples for a total of 139 chemical and other parameters. Most chemicals were not detected. Alpha HCH and chromium were detected in two samples taken at different times from the locations shown. These values represent concentrations in individual samples only, although if these concentrations are assumed to represent average concentrations, human exposure can

Table 18

Mean Concentrations and Estimated Human Exposure to Selected Persistent Toxic Chemicals Detected in Toronto's Drinking Water 1978 - 1984.

| Chemical | Average Concentration in Drinking Water[1] (ug/L) | Estimated Human Exposure (mg/a) |
|---|---|---|
| Organics | | |
| A-HCH | 0.034 | 0.025 |
| B-HCH | 0.0005 | 0.0036 |
| G-HCH | 0.0004 | 0.0003 |
| Aldrin | 0.002 | 0.0014 |
| Dieldrin | 0.001 | 0.0007 |
| DDE | 0.0003 | 0.0002 |
| Dibutyl phth. | 2.547 | 1.859 |
| Dioctyl phth. | 0.133 | 0.097 |
| Bis ethyl hexyl phth. | 63.54 | 46.38 |
| Diethyl phth. | 0.0107 | 0.0078 |
| Atrazine | 0.03 | 0.022 |
| Hexachlorobenzene | 0.002 | 0.0015 |
| Inorganics | | |
| Arsenic | 0.15 | 0.109 |
| Boron | 25.8 | 18.834 |
| Cadmium | 1.2 | 0.876 |
| Chromium | 1.8 | 1.314 |
| Cyanide | 0.81 | 0.591 |
| Mercury | 0.06 | 0.043 |
| Selenium | 0.16 | 0.116 |

Note:
A = alpha
B = beta
G = gamma
phth. = phthalate
1 = average consumption of 2 L/d (Dept. of National Health and Welfare, 1978)

Source: Davies, 1986a

## Table 19

## 1984 Concentrations of Persistent Toxic Chemicals in Drinking Water from the Niagara Area and Lake Ontario

Water Treatment Plants (ug/L)

| Chemical | Welland | St. Catherines | Niagara Falls |
|---|---|---|---|
| A-HCH | 0.004/0.003 | 0.004/0.003 | 0.005/0.004 |
| Bis ethylhexyl phth. | -/1 | -/- | -/1 |
| Chromium | 2/2 | 2/3 | 2/2 |
| Nickel | ND | 2/2 | ND |
| 1,2,4,5-tetrachlorobenzene | ND | ND | 0.009/ND |
| 1,3,5-tetrachlorobenzene | ND | ND | ND/0.005 |

| Chemical | Fort Erie | Toronto (Clark) | Hamilton | Oshawa |
|---|---|---|---|---|
| A-HCH | 0.005/0.003 | 0.006 | 0.005 | 0.004 |
| Bis ethylhexyl phth. | -/ND | ND | ND | 1 |
| Chromium | 2/2 | 3 | 3 | 2 |
| Nickel | ND | 2 | ND | ND |
| 1,2,4,5-tetrachloro-benzene | 0.004/ND | ND | ND | ND |
| 1,3,5-tetrachlorobenzene | ND | ND | ND | ND |

Note:
A = alpha
Phth. = phthalate

Source: MOE, 1984a

be estimated to be between 2.19 and 4.38 ug/a of alpha HCH, 1.46 and 2.19 mg/a of chromium and 1.46 mg/a of nickel. Samples of raw and treated drinking water were collected in 1981 and 1982 and analysed for the presence of many organic chemicals as shown in Table 20. These concentrations are all in the same range as those for Toronto.

As well as being ingested, drinking water is also used for many other purposes that could result in human exposure to persistent toxic chemicals. The most obvious of these are bathing and showering. Recent evidence suggests that many organic chemicals can be absorbed through skin (Wester et al., 1983; 1985), although the relevance of this route of exposure has not been fully assessed. The extent of absorption depends on the type of organic chemical, its concentration, the solvent and on the site and duration of dermal exposure. One study of volatile organics estimated that dermal absorption contributed between 29 and 91% of the total dose from drinking water (Brown et al., 1984). It is therefore likely that dermal exposure to persistent and toxic chemicals in drinking water contributes little to overall human exposure.

### 4.3.6 HUMAN EXPOSURE TO PERSISTENT TOXIC CHEMICALS IN AIR

The atmosphere is known to be a major direct exposure route for certain contaminants, particularly lead. Ambient atmospheric lead concentrations for several locations in Ontario in 1984 are shown in Table 21 (Ontario Ministries of Health, Labour and Environment, 1985).

## Table 20

## 1981-1982 Concentrations of Selected Organic Chemicals Detected in Treated Drinking Water from the Niagara River

| Chemical | Fort Erie (ug/1) | Niagara Falls (ug/1) | Niagara-on-the-Lake (ug/1) |
|---|---|---|---|
| A-HCH | ND-0.004 | ND-0.009 | ND-0.014 |
| G-HCH | ND | ND-0.001 | ND-0.001 |
| Heptachlor epoxide | ND | ND-0.001 | ND |
| PCB | ND | ND | ND |

Note:
ND = Not detected
A = alpha
G = gamma

Source: MOE, 1984a

## Table 21

## 1984 Ambient Atmospheric Lead Concentrations and Estimated Human Exposure in Ontario

| Location | Mean Concentration[1] ($ug/m^3$) | Estimated Human Exposure[2] (mg/a) |
|---|---|---|
| **Urban** | | |
| Windsor | 0.3 | 2.29 |
| Toronto | 0.7 | 5.33 |
| **Suburban** | | |
| Scarborough | 0.2 | 1.52 |
| Etobicoke | 0.2 | 1.52 |
| **Rural** | | |
| Nanticoke-Walpole | 0.1 | 0.76 |
| Longwoods | 0.1 | 0.76 |

Note:
1 = Ontario Ministries of Health, Labour and Environment, 1985.
2 = assumes a tidal volume of half a litre and a frequency of 29 breaths a minute

Source: Davies, 1986a.

These data suggest that there are considerable differences in the mean concentrations and estimated human exposure to lead between urban and suburban areas in Ontario. The urban areas, such as Toronto and Windsor, have higher concentrations than suburban areas, such as Scarborough and Etobicoke. There are also differences between urban and rural (Nanticoke-Walpole and Longwoods) locations. The rural locations had much lower ambient atmospheric concentrations.

Ambient atmospheric concentrations of organochlorine pesticides and PCBs in the Great Lakes basin are shown in Table 22 (Eisenreich et al., 1981). The estimated human exposure were calculated as described.

Other studies of PCB concentrations in ambient air have been conducted by the Ontario Ministry of the Environment (MOE) (Singer et al., 1983). These data are shown in Table 23.

The data in Table 23 indicate that Sarnia industrial, and the Hamilton and Toronto areas had the highest mean PCB concentrations of the locations sampled in 1979. The apparent change in the mean atmospheric concentrations of PCBs between 1979 and 1980, is due to a change in the analytical methodology used.

In a more recent study prepared for the U.S. EPA, human exposure to atmospheric PCBs was estimated to be 0.35 ug/a in rural environments and 35 ug/a in urban environments (Versar

## Table 22

## 1981 Ambient Atmospheric Concentrations and Estimated Human Exposure to Organic Chemicals in the Great Lakes Basin

| Chemical | Range[1] | Mean[1] | Estimated Human Exposure[2] |
|---|---|---|---|
| | (ng/m$^3$) | | (ug/a) |
| Total PCBs | 0.4-3.0 | 1.0 | 7.621 |
| Total DDT | 0.01-0.05 | 0.03 | 0.228 |
| A-HCH | 0.25-0.4 | 0.3 | 2.286 |
| G-HCH | 1.0-4.0 | 2.0 | 15.242 |
| Dieldrin | 0.01-0.1 | 0.05 | 0.381 |
| HCB | 0.1-0.3 | 0.2 | 1.524 |
| Total PAH | 10-30 | 20 | 152.424 |
| Anthracene | 0.1-1.0 | 0.6 | 4.572 |
| Phenanthrene | 0.1-1.0 | 0.6 | 4.572 |
| Pyrene | 0.1-4.0 | 1.1 | 8.383 |
| Benzo-a-anthracene | 0.1-1.0 | 0.5 | 3.810 |
| Perylene | 0.1-2.0 | 0.6 | 4.572 |
| Benzo-a-pyrene | 0.1-2.0 | 1.0 | 7.621 |
| Dibutyl phth. | 0.5-5.0 | 2.0 | 15.242 |
| Diethylhexyl phth. | 0.5-5.0 | 2.0 | 15.242 |

Note:
A = alpha
G = gamma
Phth. = phthalate
1 = Eisenreich et al., 1981.
2 = Assuming a tidal volume of half a litre and a frequency of 29 breaths a minute.

Source: Davies, 1986a.

### Table 23
### Mean Atmospheric Concentrations of PCBs in Ontario for 1979 and 1980

| Location | Type of Sample | 1979 Mean Concen. ($ng/m^3$) | 1979 Std. Deviation | 1980 Mean Concen. ($ng/m^3$) | 1980 Std. Deviation |
|---|---|---|---|---|---|
| Thunder Bay | Urban | 5.7 | 4.2 | 0.01 | 0.02 |
| Thunder Bay | Rural | 3.8 | 2.6 | 0.01 | 0.26 |
| Burlington | Urban | 5.6 | 5.2 | 0.10 | 0.13 |
| St. Catherines | Rural | 6.6 | 5.6 | 0.22 | 0.55 |
| Nanticoke | Rural | 5.2 | 3.2 | 0.03 | 0.04 |
| Nanticoke | Rural | 5.1 | 4.3 | 0.80 | 2.8 |
| Sarnia | Industrial | 9.8 | 9.4 | 0.28 | 0.31 |
| Sarnia | Urban | 7.3 | 5.6 | 0.10 | 0.03 |
| Moore TWP | Rural | 4.9 | 3.6 | 0.03 | 0.05 |
| Windsor | Urban | 5.6 | 3.6 | 0.06 | 0.09 |
| London | Suburban | 8.1 | 4.8 | 1.4 | 1.5 |
| Hamilton | Industrial | 7.0 | 5.6 | 0.06 | 0.07 |
| Hamilton | Industrial | 5.9 | 4.6 | 0.08 | 0.10 |
| Hamilton | Urban | 5.7 | 5.0 | 0.06 | 0.10 |
| Hamilton | Urban | 9.2 | 14.0 | 0.08 | 0.26 |
| Oshawa | Urban | 5.7 | 4.4 | 0.11 | 0.23 |
| Toronto | Suburban | 5.3 | 3.3 | 0.20 | 0.30 |
| Toronto | Urban | 9.6 | 7.3 | 0.64 | 0.89 |
| Mississauga | Urban | 5.3 | 3.9 | 0.13 | 0.18 |
| Mississauga | Urban | 5.0 | 3.9 | 0.05 | 0.06 |
| Mississauga | Urban | 6.3 | 5.7 | 0.14 | 0.12 |
| Mississauga | Urban | 5.4 | 3.6 | 0.19 | 0.20 |
| Kingston | Urban | 4.7 | 3.0 | na | na |
| Sudbury | Rural | 6.8 | 4.7 | 0.03 | 0.04 |
| Sudbury | Suburban | 4.4 | 2.9 | 0.02 | 0.03 |

Source: Singer et al., 1983.

Note: The apparent major change in concentrations between 1979 and 1980 is due to a change in analytical methodology and not the environment.

Note: na is not analysed

Inc., 1984). These EPA figures span the estimate of human exposure in the Great Lakes (Table 22). The EPA data indicate there is a two order of magnitude difference between urban and rural exposures. However the atmospheric PCB concentrations throughout Southern Ontario do not differ significantly. (Table 23).

Ambient concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans have not been determined in Ontario air.

Limited stack sampling data from municipal garbage and sewage sludge incineration in Ontario for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are available. These have been used to calculate an estimated maximum average air concentration of 2,3,7,8-TCDD or its toxic equivalent of 8.4 pg/m$^3$ near incinerators (Ozvacic et al., 1985). This is equivalent to an estimated annual individual exposure of 64 ug.

Most data on ambient atmospheric concentrations are for outdoor air. Although outdoor air is ultimately the source of all indoor air, indoor concentrations can be higher because chemicals are less able to disperse. Few studies have reported on concentrations of persistent toxic chemicals in indoor air.

### 4.3.7 HUMAN EXPOSURE TO PERSISTENT TOXIC CHEMICALS IN SOIL

The ingestion of persistent toxic chemicals in soil can be a significant route of exposure for young children. It has been estimated that up to 10 g of soil a day can be ingested, although this varies with age. Estimates of soil ingestion are shown in Table 24 (Kimborough et al., 1984). Contaminants such as PCBs in soil can also be taken up and translocated into edible plants. (Iwata et al., 1974). The concentration and type of contamination of urban and rural soils is key to understanding exposure for children.

Since pesticides are applied annually to crops and soils in order to control undesirable weeds and insects it is useful to understand the buildup of these residues in agricultural soils for comparison with industrial compounds such as PCBs. Pesticide residue levels in the U.S. have been determined as part of the National Soils Monitoring Program (Carey et al., 1978). A summary of some of the results for the Great Lakes states is shown in Table 25. Pesticide residue levels have also been determined in Ontario soil (Miles et al., 1978). This study examined insecticide residues in the organic soils from Holland Marsh, Ontario, between 1972 and 1975 (Table 26). Levels in the Holland Marsh are far higher than those estimated for the Great Lakes states, although the aldrin estimates are in closer agreement. The Holland Marsh is used extensively for vegetable production and has been heavily treated with pesticides.

## Table 24

## 1984 Estimated Ingestion of Soil by Children in the U.S.A.

| Age (yrs.) | Estimated Intake (g/d) |
|---|---|
| 0-0.75 | 0 |
| 0.75-1.5 | 1 |
| 1.5-3.5 | 10 |
| 3.5-5.0 | 1 |
| 5.0+ | 0.1 |

Source: Kimbrough et al., 1984.

## Table 25

### 1978 Mean Concentrations of Organochlorine Pesticides in Soils of the Great Lakes States.

| | Mean Concentration (mg/kg) | | |
|---|---|---|---|
| State | Aldrin | Chlordane | Total DDT |
| Illinois | 0.06 | 0.47 | ND |
| Indiana | 0.08 | 0.12 | 0.03 |
| Michigan | 0.02 | 0.02 | 0.38 |
| New York | ---- | 0.01 | 12.26 |
| Ohio | 0.01 | 0.02 | 0.76 |
| Pennsylvania | ND | ---- | 0.01 |
| Wisconsin | ---- | ND | 0.04 |
| Average | 0.03 | 0.11 | 1.92 |

| State | Dieldrin | Heptachlor | Heptachlor epoxide |
|---|---|---|---|
| Illinois | 0.14 | 0.04 | 0.02 |
| Indiana | 0.10 | 0.01 | 0.01 |
| Michigan | 0.02 | ND | ND |
| New York | 0.28 | ---- | ND |
| Ohio | 0.02 | ND | ND |
| Pennsylvania | 0.02 | ---- | ---- |
| Wisconsin | ND | ND | ---- |
| Average | 0.08 | 0.01 | 0.01 |

Note:
ND = Not detected
---- = Information not available

Source: Carey et al., 1978.

## Table 26

### Concentrations of Selected Organochlorine Insecticides in Soil from Holland Marsh 1972 - 1975

| | Total DDT | Aldrin | Dieldrin | Endrin |
|---|---|---|---|---|
| 1972$^1$ (mg/kg) | 23.7 | 0.08 | 0.92 | 0.05 |
| 1973$^1$ (mg/kg) | 30.5 | 0.11 | 1.60 | 0.09 |
| 1974$^1$ (mg/kg) | 33.8 | 0.12 | 1.56 | 0.07 |
| 1975$^1$ (mg/kg) | 26.2 | 0.06 | 1.44 | 0.09 |
| Avg. '72-'75 | 28.55 | 0.09 | 1.38 | 0.075 |

Source: Miles et al., 1978.

Ambient PCB concentrations have been determined in soil samples from one census tract in Toronto (McLoughlin, 1985). Of the 21 locations, 16 had PCB concentrations below the minimum detection level (detection level = 0.1 mg/kg). Results from the 5 sites with detectable concentrations are shown in Table 27. The average PCB concentration of the 5 sites where PCBs were detectable was 0.204 mg/kg. The estimated PCB concentration for metropolitan areas of the U.S. is approximately 0.002 mg/kg (Massachusetts Coastal Zone Management, 1982) which is less than one tenth that found in Toronto.

Background PCB concentrations in Ontario soils between 1976 - 1978 are shown in Table 28 (Webber et al., 1983). Brantford had the highest ambient PCB concentration (0.025 mg/kg) and Galt had the lowest (0.007 mg/kg). The average for all ten sites was 0.0132 mg/kg.

Soil concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans have been recently reviewed by the MOE, 1985. Ambient concentrations were below the minimum detection level (low ng/kg range) for the tetra and hepta-chloro congeners and between 0.02 - 0.05 and 0.1 - 0.2 ug/kg for the heptachloro series and the octachloro compounds, respectively, for a rural area.

In 1983, a soil sampling survey was initiated in Ontario in the vicinity of a major municipal refuse incinerator in Hamilton to determine if PCDDs and PCDFs identified in stack emissions had

## Table 27

## Concentration of PCBs in Soil Samples from Toronto (1985)

| Location | Concentration (mg/kg) |
|---|---|
| Municipal property | 0.2 |
| School playground | 0.16* |
| Residential Site 1. | 0.13 |
| Residential Site 2. | 0.35 |
| Residential Site 3. | 0.18 |

Note:
* Average of two samples

Source: McLoughlin, 1985.

## Table 28

### Ambient Concentrations of PCBs in Selected Ontario Soils (1976-1978)

| Site | Ambient Concentration (mg/kg) |
|---|---|
| Brantford | 0.025 |
| Burlington | 0.013 |
| Galt | 0.007 |
| Georgetown | 0.020 |
| Guelph | 0.012 |
| Kingston | 0.008 |
| Kitchener | 0.009 |
| Oakville | 0.015 |
| Oshawa | 0.015 |
| Stratford | 0.008 |
| AVERAGE | 0.0132 |

Source: Webber et al., 1983.

accumulated in surface soils (MOE, 1985). This study showed that all samples had detectable quantities of at least one type of chlorinated dioxin (PCDD). Soil from urban and rural control locations was also sampled and analysed. The results of these controls are shown in Table 29.

Ambient concentrations of trace metals in soil have also been studied in Ontario. One of the most prevalent metals is lead. The Ontario Ministries of Health, Labour and Environment recently reported ambient concentrations of lead in urban, suburban and rural soils (Ontario Ministries of Health, Labour and Environment, 1985). (Table 30). In both cases urban residues exceed rural values. Children are therefore exposed to a variety of toxic chemicals from soils which differ in type and concentration in urban and rural areas. In urban areas industrially derived chemicals predominate wheras in agricultural areas exposure to pesticides would most likely be highest.

### 4.3.8 REPRESENTATIVE TORONTO ADULT

Residue levels derived from the scientific literature have been used by the City of Toronto Department of Public Health to estimate the total annual human exposure and percentage exposure from fresh food, drinking water, and air (Table 31), (Davies, 1986). These estimates were based on average food expenditure statistics compiled by Statistics Canada (1984). The average concentrations from the various food and exposure routes are described in the previous sections. Where data on individual

## Table 29

### PCDD and PCDF Concentrations in Soil from Urban and Rural Areas. (1983)

| | Urban (ug/kg) | | Rural (ug/kg) |
|---|---|---|---|
| **PCDD** | | | b |
| T4 | ND | ND | ND |
| P5 | ND | ND | ND |
| H6 | ND | ND | ND |
| H7 | 0.005 | 0.097 | ND |
| O8 | 0.940 | 3.20 | 0.810 |
| TOTAL | 2.12 | | 0.81 |
| **PCDF** | | | b |
| T4 | 0.009 | 0.068 | ND |
| P5 | 0.006 | ND | ND |
| H6 | ND | ND | ND |
| H7 | ND | ND | ND |
| O8 | ND | 0.081 | ND |
| TOTAL | 0.082 | | ND |

Source: MOE, 1985a.

ND = not detected or less than the analytical detection limits which ranged from 0.0003 ug/kg for $T_4$CDDs, and 0.0013 ug/kg for all other compounds save for $O_8$CDF at 0.008 ug/kg.

## Table 30
## Ambient Soil Concentrations of Lead in Ontario

| Location | Mean Concentration (mg/kg) |
|---|---|
| **Urban** | |
| Windsor | 54 |
| Toronto | 48 |
| **Suburban** | |
| Scarborough | 20 |
| Etobicoke | 12 |
| **Rural** | |
| Longwoods | 13 |
| Walpole | 25 |
| Walpole (excl. Dunnville) | 11 |

Source: Ontario Ministries of Health, Labour and Environment, 1985.

## Table 31

## Exposure Assessment for a Representative Toronto Adult

| Chemical | Fresh Food (mg/a) | % | Drinking Water (mg/a) | % | Air (mg/a) | % | Total (mg/a) |
|---|---|---|---|---|---|---|---|
| | **Estimated Average Human Exposure** | | | | | | |
| A-HCH | 0.017 | 39.5 | 0.025 | 58.1 | 0.001 | 2.3 | 0.043 |
| G-HCH | 0.131 | 94.2 | 0.0003 | 0.2 | 0.0078 | 5.6 | 0.1391 |
| Aldrin/ Dieldrin | 1.093 | 99.7 | 0.002 | 0.2 | 0.0002 | Neg. | 1.0952 |
| Total DDT | 2.400 | 99.9 | 0.0002 | Neg. | 0.0001 | Neg. | 2.4003 |
| HCB | 0.0226 | 90.7 | 0.0015 | 6.0 | 0.0008 | 3.2 | 0.0249 |
| PCB | 0.0365 | 90.3 | ND | -- | 0.0039 | 9.6 | 0.0404 |

Note:
A = alpha hexachlorocyclohexane
G = gamma hexachlorocyclohexane or lindane

Source: Davies, 1986a.

chemicals have not been available for one or more exposure route, the chemical has not been included in the exposure assessment. Although the exposure level is generally lower because current residue values are lower, the exposure route is consistent with that estimated by Bennett (1983) previously for PCBs.

As an extension of this study Davies (1986a) also measured residue levels in fresh Ontario food composites collected from Toronto supermarkets. This study considers a more extensive series of residues including more residues derived from special waste as well as a more comprehensive food composite including fruit. The estimated annual intake percentage exposure from common organochlorine residues in the fresh food analyzed in this study is shown in Table 32, and for chlorinated dioxins and dibenzofurans in Table 33.

The series of chlorinated benzenes was most prevalent in eggs and meat followed by milk, leafy vegetables and fruit. By contrast chlorinated dioxins and dibenzofurans were very prevalent in fruit and moderately so in milk. Exposure levels from chlorinated dioxins and dibenzofurans in fruit matched or exceeded those of PCBs and DDT in fish. This exposure study is consistent with analysis of the literature and the previous exposure predictions of MacKay and Paterson (1985) for 2,3,7,8 TCDD.

A recent study from Japan found a very similar picture for PCDDs and PCDF exposure (Ono et al, 1986). Foods for seven days (21 meals) were purchased in Matsuyama during June 1986,

Table 32

## Estimated Annual Dietary Intake of Selected Persistent Toxic Organochlorine from Fresh Food Composites

| Chemical | Fruit | | Leaf Veg. | | Root Veg. | | Milk | | Eggs/Meat | | Total Est. Annual Intake (ug/a) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Est. Intake (ug/a) | % of Total | Est. Intake (ug/a) | % of Total | Est. Intake (ug/a) | % of Total | Est. Intake (ug/a) | % of Total | Est. Intake (ug/a) | % of Total | |
| Total PCBs | 11.9 | 32.6 | ---- | 0.0 | ---- | 0.0 | 6.6 | 18.1 | 18.0 | 49.3 | 36.5 |
| a-HCH | 0.3 | 1.8 | ---- | 0.0 | ---- | 0.0 | 8.6 | 51.5 | 7.8 | 46.7 | 16.7 |
| g-HCH | 1.7 | 1.3 | 2.1 | 1.6 | 1.5 | 1.1 | ---- | 0.0 | 126.0 | 95.9 | 131.3 |
| Heptachlor epoxide | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 13.9 | 65.8 | 7.2 | 34.1 | 21.1 |
| Dieldrin | 1.9 | 0.2 | 94.9 | 8.7 | 684.5 | 62.6 | 125.8 | 11.5 | 186.0 | 17.0 | 1093.1 |
| a-Chlordane | 2.2 | 11.6 | ---- | 0.0 | 3.0 | 15.8 | 6.6 | 34.7 | 7.2 | 37.9 | 19.0 |
| g-Chlordane | 1.0 | 18.7 | 1.8 | 34.3 | 1.2 | 22.5 | 1.3 | 24.4 | ---- | 0.0 | 5.3 |
| Oxychlordane | ---- | 0.0 | 1.2 | 8.5 | ---- | 0.0 | 5.3 | 37.0 | 7.8 | 54.5 | 14.3 |
| a-Endosulfan | 23.9 | 17.0 | 116.3 | 83.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 140.1 |
| b-Endosulfan | 97.1 | 12.4 | 520.2 | 66.3 | 21.1 | 2.7 | 145.6 | 18.6 | ---- | 0.0 | 784.0 |
| Endrin | 4.6 | 10.6 | 9.8 | 22.6 | 11.0 | 25.4 | 17.9 | 41.4 | ---- | 0.0 | 43.3 |
| o,p'-DDT | ---- | 0.0 | 0.6 | 100.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 0.6 |
| p,p'-DDT | 6.6 | 0.3 | 12.9 | 0.6 | 1934.4 | 93.6 | 92.7 | 4.5 | 18.6 | 0.9 | 2065.2 |
| p,p'-DDE | 78.4 | 26.1 | 6.1 | 2.0 | 11.6 | 3.8 | 17.9 | 6.0 | 186.0 | 62.0 | 300.0 |
| p,p'-DDD | ---- | 0.0 | 10.4 | 30.0 | 14.0 | 40.5 | ---- | 0.0 | 10.2 | 29.5 | 34.6 |
| 1,3-Dichlorobenzene | 75.0 | 37.4 | ---- | 0.0 | 32.7 | 16.3 | 92.7 | 46.3 | ---- | 0.0 | 200.4 |
| 1,4-Dichlorobenzene | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 364.1 | 100.0 | ---- | 0.0 | 364.1 |
| 1,2-Dichlorobenzene | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 108.0 | 100.0 | 108.0 |
| 1,3,5-Trichlorobenzene | 2.0 | 1.6 | 8.6 | 6.5 | ---- | 0.0 | 79.4 | 60.2 | 42.0 | 31.8 | 132.0 |
| 1,2,4-Trichlorobenzene | 2.4 | 3.8 | 12.2 | 18.0 | ---- | 0.0 | 9.3 | 13.6 | 44.4 | 64.9 | 68.4 |
| 1,2,3-Trichlorobenzene | ---- | 0.0 | 3.4 | 100.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 3.4 |
| Hexachlorobenzene | ---- | 0.0 | 0.6 | 2.7 | 1.2 | 5.3 | 10.6 | 46.9 | 10.2 | 45.1 | 22.6 |

Source: Davies, 1986a.

## Table 33

### Estimated Dietary Intake of PCDDs and PCDFs from Fresh Food Composites

| Chemical | Fruit | | Leaf Veg. | | Root Veg. | | Milk | | Eggs/Meat | | Total Est. Annual Intake (ug/a) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Estimated Intake (ug/a) | % of Total | Estimated Intake (ug/a) | % of Total | Estimated Intake (ug/a) | % of Total | Estimated Intake (ug/a) | % of Total | Estimated Intake (ug/a) | % of Total | |
| T4CDF | 0.77 | 6.5 | ---- | 0.0 | ---- | 0.0 | 7.94 | 67.8 | 3.00 | 25.6 | 11.71 |
| T4CDD | ---- | 0.0 | 0.01 | 5.8 | ---- | 0.0 | 0.16 | 94.1 | ---- | 0.0 | 0.17 |
| P5CDF | 4.77 | 76.6 | ---- | 0.0 | ---- | 0.0 | 0.50 | 8.0 | 0.96 | 15.4 | 6.23 |
| P5CDD | 0.08 | 100.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 0.08 |
| H6CDF | 34.08 | 99.8 | ---- | 0.0 | 0.06 | 0.2 | ---- | 0.0 | ---- | 0.0 | 34.14 |
| H6CDD | 7.67 | 100.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | ---- | 0.0 | 7.67 |
| H7CDF | 112.46 | 98.2 | ---- | 0.0 | 1.16 | 1.0 | 0.86 | 0.8 | ---- | 0.0 | 114.48 |
| H7CDD | 20.45 | 97.2 | ---- | 0.0 | 0.36 | 1.7 | 0.22 | 1.0 | ---- | 0.0 | 21.03 |
| O8CDF | 20.45 | 72.3 | ---- | 0.0 | 3.9 | 13.7 | 3.84 | 13.6 | 0.11 | 0.4 | 28.3 |
| O8CDD | 2.04 | 43.2 | ---- | 0.0 | 0.3 | 6.4 | 2.38 | 50.4 | ---- | 0.0 | 4.72 |

Source: Davies, 1986a.

according to the standard energy and food compositions for Japanese. These food items were grouped into eight categories: vegetables, plant oil, rice and wheat, fish, beef, pork, chicken, and egg. Each categorical sample was mixed and analyzed for PCDDs/PCDFs respectively.

PCDDs/PCDFs were detected at ng/kg levels from all categories analyzed. The daily intake of PCDDs/PCDFs was estimated to be about 4000 pg (egg, 1100 pg; vegetables, 880 pg; chicken, 540 pg; pork, 450 pg; plant oil, 230 pg; rice + wheat, 220 pg; fish, 170 pg; and beef, 27 pg). The total 2,3,7,8-TCDD equivalents from the daily intake from food were calculated to be 45 pg/man/day (egg, 13.7 pg; fish, 11.9 pg; vegetables, 8.3 pg; chicken, 8.0 pg; rice + wheat, 2.3 pg; pork, 0.4 pg; beef, 0.3 pg; and plant oil, 0.1 pg) or 0.9 pg/kg body weight/day for a person weighing 50 kg.

Vegetables were a major source of tetra-CDDs in foods, accounting for 55% of the daily intake. Hexa- and hepta-CDDs in foods mainly came from chicken and eggs. Octa-CDD was detected only in pork and was 9% of the daily intake of PCDDs/PCDFs.

In light of the above studies human body burdens of organochlorine residues, including chlorinated dioxins and dibenzofurans derived from special waste such as those shown in Table 8 (pg. 72) are most likely derived from exposure through food. The human food chain is contaminated in a similar fashion to the food chains of wildlife and fish.

## 4.4 DISCUSSION

Persistent residues such as PCBs, chlorinated benzenes, chlorinated dioxins and furans, and mercury originating from special waste have long been considered a problem for fish and wildlife, particularly fish-eating birds such as bald eagles, herring gulls, cormorants and loons. These persistent residues are well known to bioaccumulate up aquatic food chains increasing in concentration and exposing these top food chain feeders to a continuous high residue intake. The primary human exposure route to environmentally based residues of PCBs, chlorinated benzenes, and chlorinated dioxins and furans has been shown to be food consumption.

The major contaminant groups of concern derived from food are chlorinated dioxins and dibenzofurans which are most prevalent in Ontario fruit and milk. PCBs, and chlorinated benzenes are also prevalent in food. Chlorophenols are the predominant organochlorine residues in Ontario milk. Other environmental residues found in food still consist of persistent pesticides such as DDT, or dieldrin and heptachlor which although severely restricted for over a decade are still present in heavily dosed agricultural soils and the crops harvested from them.

Fish are the primary source of human exposure for many of the latter compounds. However meat, pork, chicken, eggs, milk, fruit and vegetables are the other major sources before air and drinking water.

Certain compounds present a more significant exposure via drinking water. These include special waste residues such as bis ethyl hexyl phthalate and other phthalate esters which are plasticizers; trace metals such as boron; and insecticides such as alpha hexachlorocyclohexane, a byproduct contaminant associated with lindane. The air can be a major exposure route for lead.

Current exposure to the compounds mentioned in this study do not exceed the Maximum Residue Limits (MRLs) established in the Canadian Food and Drug Act (Davies, 1986a). On the other hand, MRLs for chlorinated dioxins and dibenzofurans and for many of the chlorinated benzene compounds have not been established under this Act because of inadequate information about the toxicology, the environmental occurrence and the human multimedia exposure routes. The MRLs available for compounds such as PCBs have not fully considered multimedia exposure routes since only recent data and studies have considered all types of food in exposure estimates.

Soil must be considered in certain urban areas as a concern either for ingestion by children or for urban gardening. Compounds such as dioxin, PCBs and lead are of concern in urban soil.

Finally, residues in mothers' milk must be considered since there has been a large increase in national breast-feeding trends from 38% of mothers in 1963 to 75% in 1982 (Frank, 1986) and the number of months of breast-feeding has also increased. Residues of concern in mothers' milk include PCBs, chlorobenzenes, and chlorinated dioxins and dibenzofurans (Rappe, 1986). Breastfed newborns rely on mothers' milk as a sole source of food and are exposed to intake rates which far exceed those of an adult during a period of rapid tissue and organ development. A similar situation exists for non-breastfed infants except that the residue burden and exposure rate is approximately 10 times lower since cows' milk and other infant formulae are not without contamination.

Humans from the day they are born are continually exposed to levels of toxic chemicals derived from special waste via their food at levels which have either yet to be assessed toxicologically or have yet to be assessed while considering multimedia exposure routes. At worst the multiple chemical effect from multiple exposure routes and the continual buildup of biological stress as has been described in chapters 2 and 3 for fish and wildlife has not been studied in humans, and it is very doubtful that definitive experiments can ever be developed to prove safety or lack of it in humans. The human residue exposure levels currently documented, reflect environmental exposures largely from the atmospheric pathway. Residue burdens in humans are within a factor of 100 of those found in wild species currently exhibiting chronic disease. It therefore seems most likely that chronic effects leading up to disease are occurring in the human population as well, particularly in those critical subpopulations predisposed to toxic chemical related disease, or in those populations with increased occupational exposure.

## 4.5 MAJOR FINDINGS

1. Ecosystem Pathways and Human Exposure Routes to Special Waste.

a) Ontario citizens are exposed to and are bioaccumulating the same residues derived from special waste as those present in wild populations.

b) Levels of chlorinated dioxins in human body fat sampled to date are equivalent to those found in Lake Ontario alewives and smelt and are within a factor of 10 to 100 of those found in populations of fish and birds experiencing population-wide effects.

c) The main exposure route to humans in Ontario of these residues from special waste such as PCBs or chlorinated dioxins is via food grown in Southern Ontario.

d) The food derived from the Ontario terrestrial ecosystem (cropland) is contaminated via the atmosphere in the same fashion as the fisheries resource derived from the Great Lakes aquatic ecosystem is contaminated via the atmosphere.

e) Exposure routes such as drinking water supplies in major Ontario cities represent such a minor route of exposure that mitigation of human exposure through treatment of drinking water would not significantly reduce the current human exposure to toxic chemicals derived from special waste.

f) The elevated exposure rate or dosage of certain human sub-populations such as newborns, children or occupationally exposed groups is more critical.

g) Removal of the sources of special waste which stem from improper disposal and treatment appears to be the only practical and effective solution.

# CHAPTER 5

# SOURCES OF PRIORITY CHEMICALS

## 5.1 INTRODUCTION

The most obvious sources of environmental contaminants of industrial origin occur at either their production or during their use. These sources are regulated currently under federal acts such as the Environmental Contaminants Act, the Fisheries Act, and provincially under the Environmental Protection Act. However, many other less obvious but far larger sources of these chemicals to the environment exist. These sources include spills, municipal treatment plants, and atmospheric sources which occur due to present waste treatment practices.

The previous four chapters have dealt with an analysis of the detrimental effects caused by exposure to toxic chemicals derived from special waste and the environmental pathways by which these exposures occur. This chapter deals with the major sources to these environmental pathways.

## 5.2 INDUSTRIAL SOURCES

Industrial sources of environmental toxic chemicals derived from special waste can be broken down by sector into iron and steel, pulp and paper, petrochemical, manufacturing, and service industries such as food processing.

A good cross section demonstrating major Ontario industrial effluent loadings from various sectors is found on the Niagara River. The major industrial discharges can be compared with the effluents from municipal waste pollution control plants (WPCPs) and combined sewer overflows (CSOs). The gross loadings of priority pollutants from the 9 major Ontario dischargers to the Niagara River are shown in Table 34.

A list of 13 metals, 115 organic compounds and cyanide was compiled by the US EPA and was termed the Priority Pollutant List in a 1976 US Court Consent Decree. These contaminants are most actively researched and represent the best data base in industrial and municipal effluents. Of the total priority pollutant loading from all Canadian point sources (154.9 kg/d), 8 significant sources accounted for 97% of the organics, 99% of the metals, 98% of the cyanide and 97% of the total phenols. The discharges from water pollution control plants and combined sewer overflows are the major sources of loading after Atlas Steels (Table 34). Table 35 lists the major sources and the most significant pollutants. Heavy metals were most prevalent particularly at Atlas Steels. These parameters are generally found at much higher concentrations than trace organics and they

## Table 34

## Canadian Point Sources To The Niagara River

| Significant Sources | kg/d[1] | Minor Sources | kg/d[1] |
|---|---|---|---|
| 1. Atlas Steels | 73.9 | 1. Stanley Ave. CSO | 1.11 |
| 2. Niagara Falls WPCP | 23.7 | 2. Norton Company | 0.384 |
| 3. Welland WPCP | 17.8 | 3. Gould Manufacturing | 0.346 |
| 4. McMaster Ave. CSO | 13.8 | 4. Canadian Carborundum | 0.205 |
| 5. Cyanamid Canada Ltd. (Welland Plant) | 12.7 | 5. Stelco Welland Tubes | 0.195 |
| | | 6. B.F. Goodrich | 0.145 |
| 6. Fort Erie WPCP | 7.03 | 7. Ford Glass Plant | 0.0995 |
| 7. Cyanamid Canada Ltd. (Niagara Plant) | 2.08 | 8. Holiday Farms | 0.0443 |
| | | 9. Canadian Oxy Chemicals | 0.0387 |
| 8. Fleet Manufacturing | 1.27 | | |

[1] Total Gross loadings of priority pollutants (Total Canadian point source loading to the Niagara was 154.4 kg/d)

Source: MOE, 1985c

Table 35

Major Canadian Point Sources To The Niagara River And Significant Loading Parameters

| Point Source | Parameter | Loading (kg/d) |
|---|---|---|
| 1. Atlas Steels | Chromium | 32.64 |
| | Copper | 1.36 |
| | Lead | 4.62 |
| | Nickel | 27.2 |
| | Zinc | 4.35 |
| | Trichloroethylene | 3.04 |
| 2. Niagara Falls WPCP | Phenols (4AAP) | 0.87 |
| | Chromium | 3.57 |
| | Copper | 0.93 |
| | Lead | 0.57 |
| | Zinc | 11.3 |
| | Methylene chloride | 0.39 |
| | Cyanide | 0.34 |
| | 2,4-Dichlorophenol | 0.39 |
| | Dibutylphthalate | 3.40 |
| | Diethylphthalate | 0.79 |
| | Bis (2-ethylhexyl) Phthalate | 0.30 |
| 3. Welland WPCP | Copper | 0.70 |
| | Lead | 13.4 |
| | Zinc | 1.71 |
| 4. McMaster Ave Combined Sewer | Phenols (4AAP) | 0.37 |
| | Chromium | 2.2 |
| | Copper | 1.01 |
| | Lead | 4.64 |
| | Nickel | 3.56 |
| | Zinc | 1.37 |
| | Di-n-butylphthalate | 0.26 |
| | Bis(2-ethylhexyl) Phthalate | 0.27 |
| 5. Cyanamid Canada (Welland Plant) | Chromium | 4.87 |
| | Nickel | 2.34 |
| | Zinc | 2.04 |
| | Copper | 0.65 |
| | Cyanide | 2.29 |
| 6. Fort Erie WPCP | Phenols (4AAP) | 0.27 |
| | Copper | 0.49 |
| | Zinc | 1.30 |
| | 1,2-Dichloroethane | 0.32 |
| | Trans-1,2-Dichloroethene | 1.79 |
| | Dimethyl Phthalate | 0.75 |
| | Dibutyl Phthalate | 0.99 |
| 7. Cyanamid Canada (Niagara Falls) | Zinc | 0.60 |
| | Cyanide | 0.96 |
| | Butyloctyl Phthalate | 0.35 |
| 8. Fleet Manufacturing | Chromium | 1.08 |

Source: MOE, 1985c

accounted for 88.5% of the total Canadian point source loading. The WPCPs and CSOs were the primary sources of organic pollutants. The latter require better management first by removing the points of entry of special waste into these systems and by providing for proper treatment or destruction if necessary.

Atlas Steels was the only Canadian point source among the top 10 dischargers of total priority pollutants from both American and Canadian sides of the Niagara River and ranked fifth. The Atlas Steel loading was mainly due to metals and are reported to have been reduced since the publication of these data as a result of the installation of a waste acid solidification plant. On the basis of organic priority pollutants, the Niagara Falls WPCP, Fort Erie WPCP and Atlas Steels ranked 8th, 9th and 10th respectively. Atlas was also fifth among the top 10 dischargers of inorganic priority pollutants.

Among the individual pollutant parameters, five metals (chromium, copper, lead, nickel and zinc) accounted for 99% of the priority metals loading from Canadian point sources. Fifteen organic pollutants accounted for 96% of the Canadian organic priority pollutant loading. The organic pollutants are listed in Table 36.

Relatively volatile but persistent priority pollutants are the most frequent on this list. The three municipal WPCPs discharged 51% of the total volatile chemicals from Canadian point sources and Atlas Steels an additional 40% of the total Canadian loading. The three WPCPs accounted for 98% of the total

Canadian point source loading of acid extractables with 2,4-dichlorophenol and phenol the major pollutants. Low levels of PAHs were discharged with naphthalene making up 60% of the Canadian total. PCBs were detected in five effluents (Gould, Holiday Farms, Welland WPCP, Cyanamid Welland Plant and the Ford Glass Plant), for a total loading of 0.0063 kg/d, mainly from the Welland WPCP (91%). Phthalates (97% of category loading) were also frequent in the list of 15 organics presented above. The three municipal WPCPs and the McMaster Ave. sewer discharged 86% of the total "other base/neutrals" from Canadian point sources. Industrial discharge via WPCPs and CSOs is obviously an importance source and will be detailed later.

## 5.3 PETROLEUM REFINERIES

A variety of types of wastes are produced in Canadian refineries. According to the Canadian Petroleum Refining Industry Waste Survey, (Env. Canada, 1979), 196 000 t/a of total waste is generated across Canada by the refining industry. Of this total, 61 800 t/a are in the form of solids or semisolid waste expressed on a dry basis and 69 000 t/a are aqueous wastes comprised mainly of spent acids and caustics. The oil content of disposed wastes is 6 200 t/a or approximately .01% of the average crude refinery rate for 1979.

## Table 36

## Primary Loadings of Priority Pollutants Into The Niagara River From Ontario Sources

| | PARAMETER | kg/d |
|---|---|---|
| 1. | Di-n-butyl phthalate | 5.3 |
| 2. | Trichloroethylene | 3.3 |
| 3. | trans-1, 2-dichloroethylene | 1.9 |
| 4. | diethyl phthalate | 1.1 |
| 5. | bis-(2-ethylhexyl)phthalate | 0.93 |
| 6. | methylene chloride | 0.91 |
| 7. | dimethyl phthalate | 0.75 |
| 8. | toluene | 0.57 |
| 9. | butylbenzyl phthalate | 0.43 |
| 10. | 1,2-dichloroethane | 0.40 |
| 11. | 2,4-dichlorophenol | 0.39 |
| 12. | chloroform | 0.34 |
| 13. | benzene | 0.25 |
| 14. | 1,1,1-trichloroethane | 0.25 |
| 15. | 1,2-dichlorobenzene | 0.24 |

Source: MOE, 1985c

In 1981 approximately 40 300 t of solid wastes were generated by Ontario refineries. Six refineries have their own surface biodegradation sites. A summary of current waste disposal practices employed by Ontario refineries is presented in Table 37. Landspreading is particularly important for sludges and is the second most frequently used on a total dry weight basis. The current trend for the disposal of sludges and liquid oily wastes is to design soil surface degradation areas within refinery property to meet company specifications and Ontario environmental protection standards.

Oil sludges can vary in composition from almost no hydrocarbon components (biosludges) to moderately high hydrocarbon content (tank bottom sludge). Compared with municipal sewage sludges, refinery biosludges have similar content of metals such as copper, chromium, and mercury; more cadmium and vanadium; and less zinc, lead, nickel, and manganese.

Refinery effluents contain many priority pollutants all of which are derived from special waste (Table 38). The highest frequency of detection was for chlorinated solvents such as methylene chloride, byproducts of solvent synthesis such as hexachlorobenzene and less common metals such as arsenic, chromium and copper. Sludges from which these effluents are derived would contain these compounds in higher concentrations.

## Table 37

## Summary of Waste Disposal Methods - Ontario Refineries

| Waste | Disposal Method |
|---|---|
| Spent catalysts | Sold to refineries, used in cement, secure landfill |
| Spent caustic | Neutralize effluents, sold for phenol recovery |
| Leaded sludge | On-site landspreading* |
| API sludge | On-site landspreading, offsite secure landfill |
| Biological sludge | On-site landspreading, offsite landfill |
| Desalter sludge | On-site landspreading |
| Off spec. sulphur | Recovery, sale, landfill |
| Tank bottoms | Landfill, landspreading |

* Leaded sludges are disposed of in their own government approved areas.

Source: IJC, 1982b

## Table 38

### Frequency Of Detection And Mean Concentration Of Priority Pollutants Detected In Refinery Final Effluents

| Priority Pollutant | Frequency Of Detection | Mean (ug/L) |
|---|---|---|
| PURGEABLE GROUP | | |
| Benzene | 7 (50%) | 226 |
| Carbon Tetrachloride | 4 (29%) | 6.7 |
| Chloroform | 11 (79%) | 10.7 |
| 1,1-Dichloroethane | 2 (14%) | 6.0 |
| 1,2-Dichloroethane | 2 (14%) | 78.0 |
| 1,2-Dichloropropane | 2 (14%) | 9.5 |
| Ethylbenzene | 4 (29%) | 7.2 |
| Methylene Chloride | 12 (86%) | 45.1 |
| Toluene | 8 (57%) | 208 |
| 1,1,1-Trichloroethane | 5 (36%) | 2.7 |
| Trichlorofluoromethane | 2 (14%) | 5.1 |
| BASE NEUTRAL GROUP | | |
| Acenaphthene | 1 (7%) | Trace |
| Acenaphthalene | 1 (7%) | Trace |
| Anthracene | 2 (14%) | 0.13 |
| Benzo(a)Anthracene | 3 (21%) | 4.2 |
| Benzo(k)Fluoranthene | 4 (29%) | 0.10 |
| Chrysene | 4 (29%) | 1.3 |
| Fluorene | 3 (21%) | 2.4 |
| Naphthalene | 8 (57%) | 7.3 |
| Phenanthrene | 4 (29%) | 3.6 |
| Pyrene | 5 (36%) | 0.9 |
| Di-n-butylphthalate | 1 (7%) | Trace |
| Diethylphthalate | 2 (14%) | 16.5 |
| Dimethylphthalate | 1 (7%) | 14 |
| bis-(2-Ethylhexyl) Phthalate | 4 (29%) | 11.1 |
| bis-(2-Chloroisopropyl) Ether | 1 (7%) | 37 |
| ACID GROUP | | |
| Phenol | 6 (43%) | 162 |
| PESTICIDE GROUP | | |
| Polychlorinated Biphenyls | 3 (21%) | 0.20 |
| Hexachlorobenzene | 9 (65%) | 0.03 |

## Table 38 (cont'd)

## Frequency Of Detection And Mean Concentration Of Priority Pollutants Detected In Refinery Final Effluents

| Priority Pollutant | Frequency Of Detection | Mean (ug/L) |
|---|---|---|
| METALS | | |
| Arsenic | 12 (86%) | 0.006 |
| Cadmium | 1 (7%) | 0.001 |
| Chromium | 12 (86%) | 0.19 |
| Copper | 14 (100%) | 0.013 |
| Iron | 14 (100%) | 0.60 |
| Lead | 10 (71%) | 0.007 |
| Mercury | 4 (29%) | 0.0004 |
| Nickel | 8 (57%) | 0.015 |
| Selenium | 9 (64%) | 0.007 |
| Zinc | 14 (100%) | 0.085 |
| Barium | 14 (100%) | 0.092 |
| Boron | 14 (100%) | 0.27 |
| Manganese | 14 (100%) | 0.073 |
| MISC. PARAMETERS | | |
| Fluoride | 14 (100%) | 3.58 |
| Cyanide | 5 (36%) | 0.07 |
| Total Organic Carbon | 14 (100%) | 44 |
| Ammonia Nitrogen | 14 (100%) | 6.08 |
| Sulphide | 6 (43%) | 1.77 |
| Total Phenols | 14 (100%) | 2.04 |
| Oil and Grease | 9 (64%) | 7.8 |

FREQUENCY OF DETECTION = Defined as the number of samples in which the substance in question was detected based on 14 final effluent samples. Percentage given in brackets.

Source: IJC, 1982b

The disposal of special waste from petroleum refineries is therefore a source of many persistent organic and metallic chemicals that are present in the environment today. The evaporation or volatilization of organic compounds into the air from current sludge disposal techniques particularly by landspreading may be a significant atmospheric source. Refinery waste is therefore a major source of special waste requiring better management.

## 5.4 PULP AND PAPER

Recent surveys of pulp and paper mill effluents show long lists of organic and inorganic constituents. Those chemicals which appear in Appendices 1 and 2 of the Great Lakes Water Quality Agreement are included in Table 39. This Table forms the basis of the following discussion largely taken from the IJC Pulp and Paper Point Source Task Force Report (IJC, 1981).

A few of the constituents of pulp and paper mill effluents (e.g. chlordane and DDT) have been identified as contaminants from their past usage in agriculture and forestry. Two others, ammonia and phosphorus, are commonly added nutrients to assist in the biological treatment of pulp and paper mill wastes. Treated effluents are usually low in ammonia and phosphorus; however, overdosing sometimes occurs.

## Table 39

### Compounds Found in Pulp and Paper Mill Effluents Which Appear in Appendix 1 or Appendix 2 of the Great Lakes Water Quality Agreement

| APPENDIX 1 | APPENDIX 2 |
|---|---|
| Ammonia | Cadmium |
| Benzene | Chromium |
| Mercury | Copper |
| Chlordane | Dibutyl phthalate |
| Chlorobenzene | |
| Chloroform | |
| Cresol | |
| DDT | |
| Lead | |
| Naphthalene | |
| Nickel | |
| Pentachlorophenol | |
| Phenolics | |
| Phosphorus | |
| PCBs | |
| Selenium | |
| Toluene | |
| Trichlorophenol | |
| Xylene | |
| Zinc | |

Source: IJC, 1981a

Three phenolic compounds: phenol, pentachlorophenol, and trichlorophenol which appear in Appendix 1 of the Agreement are found in the pulp and paper effluents. Phenolics are found in the effluents as a result of the partial or complete breakdown of the larger lignin phenolic polymer during the cooking or bleaching process. Chlorinated phenols are noted for causing tainting problems in fish, and taste and odour problems in public water supplies. In addition, both pentachlorophenol and trichlorophenol are known to be contaminated with certain dioxins and these compounds have recently been found in over 12 plant effluents (USEPA, 1986). Due to their persistence, toxicity, and bioaccumulation potential, these dioxins may pose an environmental threat even at low levels. Both United States and Canadian agencies are aware of these problems and are planning to regulate the discharge of chlorinated phenolic compounds more closely in the future. The sodium salts of these compounds have not been registered in Canada as a fungicide or slimicide in the pulp and paper industry since January, 1981. However, the sodium pentachlorophenate may still be found in coating clays, for instance, and are unlikely to be found in the effluent. The U.S. EPA has proposed that the use of trichlorophenol and pentachlorophenol salts be prohibited and other compounds be used in their place. While it has been suggested that these compounds are also formed during the bleaching process, both Canadian and

Based upon octanol/water partition coefficients, benzene, ethylbenzene, methylbenzene, and nitrobenzene should bioaccumulate only slightly. Because these compounds are volatile, levels should be kept below concentrations which may cause acute or chronic toxicity to aquatic life. The chlorinated benzenes may present a different problem since they have a high lipid solubility and are expected to accumulate in ecosystems.

Naphthalene, also widely used by industry in formulating solvent lubricants and in producing dye compounds, occurs in pulp and paper mill effluents. Naphthalene can oxidize in light and air, and some microorganisms can degrade naphthalene ultimately to carbon dioxide and water. Thus, good biological treatment may be effective in removing naphthalene.

PCBs are another class of chlorinated organics which are found in some mill discharges, particularly those using recycled paper (deinking mills). PCBs were used in "no-carbon-required" paper in the late 1960s and early 1970s. When such paper was recycled the PCBs contaminated other papers. The use of PCBs in this paper was discontinued in the early 1970s. However, PCBs continue to be found in discharges from mills using recycled paper due to residual contamination.

Recent measurements of PCB concentrations at Wisconsin mills which recycle paper indicate that one large mill with only 1-3 ug/L of PCB in the effluent will discharge approximately 23-45 kg/a of PCBs into Lake Michigan. Pulp and paper mill effluents as well as the disposal of sludges derived from treatment of waste streams are therefore another source of toxic chemicals derived from special waste. Since further treatment of effluents will likely concentrate more contaminants in sludge, perhaps the sludges from pulp and paper mills are a major type of special waste requiring close management.

## 5.5 MUNICIPAL WASTEWATER TREATMENT PLANTS

As discussed in Section 5.2, on Industrial Sources, much industrial waste enters the environment from waste pollution control plants and combined sewer outfalls. Industrial sectors which discharge appreciable amounts of toxic substances in their wastewater streams to municipal treatment facilities are shown in Table 40.

Many municipalities in the U.S.A. have recognized the threat posed to the stability of the operation of their wastewater treatment plants by metals and other special wastes and have instituted or considered pretreatment requirements for them under local bylaws. This waste will have to be treated by other means. A survey of municipal treatment plants has shown that metals do occur in effluents at concentrations which are of concern and close monitoring of influent metals is necessary to ensure the stability of biological treatment systems.

## Table 40

## Major Industry Categories Which Are Significant Sources of Toxic Substances and Potential Discharges to Municipal Sewage

Auto and Other Laundries
Coal Mining
Electroplating
Inorganic Chemicals Manufacturing
Iron and Steel Manufacturing
Leather Tanning and Finishing
Machinery and Mechanical Products
Aluminum Forming
Battery Manufacturing
Coil Coating
Copper Forming
Electrical and Electronic Components
Foundries
Metal Finishing
Photographic Equipment and Supplies
Plastics Processing
Porcelain Enameling
Adhesives and Sealants
Explosives Manufacture
Gum and Wood Chemicals
Pesticide Manufacturing
Pharmaceutical Manufacturing
Nonferrous Metals Manufacturing
Ore Mining and Dressing
Organic Chemicals Manufacturing
Paint and Ink Formulation
Petroleum Refining
Plastic and Synthetic Materials Manufacturing
Pulp and Paperboard Mills and Converted Products
Rubber Processing
Soap and Detergent Manufacturing
Textile Mills
Timber Products Processing

Source: IJC, 1983b

Table 41 presents data on the most frequently detected organic priority pollutants from a study conducted in 1978 by the University of Washington and the Georgia Institute of Technology to also provide an overview of presence and removal of organic priority pollutants at wastewater treatment plants in 25 U.S. cities. Plant flows ranged from 13 200 to 1 170 000 $m^3$/d (3.5 to 309 MGD), while the proportion of industrial flow varied from 0 to 60 percent. A majority of the plants used an activated sludge process; however, trickling filter and aerated lagoon systems were also included in the survey.

The capacity of these treatment processes to remove organic contaminants from the wastewater streams is indicated. However, as would be expected, the chemicals are concentrated in the sludge (Table 42). The presence of organic contaminants in the sludge has raised concerns with regard to the appropriate disposal of this material and additional research is needed to address these concerns.

The compounds identified are clearly associated with chemical manufacturing, electrical and product finishing type industries which commonly discharge wastes to sanitary sewer systems. The data available for Canadian sewage treatment plants are comparable to the larger data base available for U.S. plants.

The major problem chemicals carried into municipal treatment plants and subsequently discharged in their effluents are

## Table 41

## Most Frequently Detected Organic Priority Pollutants in Influent, Effluent and Sludge Samples

(25 U.S. cities)

| | PERCENT OCCURRENCE AT INDICATED CONCENTRATIONS | | | | | |
|---|---|---|---|---|---|---|
| | INFLUENT | | | EFFLUENT | | |
| COMPOUND | >1ug/L | >10ug/L | >50ug/L | >1ug/L | >10ug/L | >50ug/L |
| Methylene chloride | 83 | 57 | 33 | 79 | 41 | 28 |
| Chloroform | 74 | 26 | 3 | 55 | 6 | 0 |
| 1,1,1-trichloroethane | 90 | 61 | 16 | 53 | 22 | 6 |
| Trichloroethylene | 90 | 61 | 19 | 47 | 16 | 3 |
| Tetrachloroethylene | 94 | 65 | 26 | 77 | 19 | 3 |
| 1,4-dichlorobenzene | 83 | 37 | 6 | 38 | 6 | 0 |
| Ethylbenzene | 87 | 23 | 13 | 13 | 3 | 0 |
| Toluene | 84 | 61 | 23 | 45 | 17 | 3 |
| Phenol | 86 | 66 | 31 | 38 | 6 | 3 |
| Naphthalene | 86 | 37 | 11 | 24 | 3 | 0 |
| Phenanthrene | 57 | 9 | 0 | 15 | 3 | 0 |
| Diethyl phthalate | 91 | 57 | 17 | 62 | 29 | 0 |
| Di-n-butyl phthalate | 89 | 60 | 9 | 85 | 18 | 3 |
| Bis(2-EH) phthalate | 86 | 69 | 20 | 76 | 38 | 6 |
| Butyl benzyl phthalate | 77 | 60 | 11 | 32 | 15 | 0 |

Source: IJC, 1983b

## Table 42

## Most Frequently Detected Organic Priority Pollutants in Sludge Samples

| | PERCENT OCCURRENCE AT INDICATED CONCENTRATIONS | | |
|---|---|---|---|
| | | SLUDGE | |
| COMPOUND | >1ug/L | >10ug/L | >50ug/L |
| Methylene chloride | 41 | 12 | 3 |
| Chloroform | 3 | 0 | 0 |
| 1,1,1-trichloroethane | 5 | 3 | 0 |
| Trichloroethylene | 26 | 9 | 3 |
| Tetrachloroethylene | 27 | 8 | 3 |
| 1,4-dichlorobenzene | 36 | 18 | 5 |
| Ethylbenzene | 33 | 3 | 0 |
| Toluene | 59 | 35 | 11 |
| Phenol | 63 | 25 | 13 |
| Naphthalene | 65 | 33 | 15 |
| Phenanthrene | 60 | 20 | 8 |
| Diethyl phthalate | 43 | 23 | 13 |
| Di-n-butylphthalate | 63 | 25 | 13 |
| Bis(2-EH)phthalate | 75 | 63 | 25 |
| Butyl benzyl phthalate | 50 | 35 | 18 |

Source: IJC, 1983b

summarized in Table 43. Although general loading information for Ontario is not available it is obvious that municipal sewage treatment plants and combined sewer overflows receive major loadings of special waste (Craig, 1985). Not only are the effluents currently a problem as shown in the Niagara River (Section 5.1) but the disposal of the contaminated sludge created is perhaps more difficult. Proper treatment of this special waste before it enters the sewer and the availability of Best Available Technology for treatment and disposal of waste residues would remove both problems.

## 5.6 SPILLS

Spills are very significant sources of special waste into the environment. Spills are accidental industrial or municipal discharges of untreated waste chemicals which occur through mechanical failures, human errors, or acts of God such as severe rainstorms which exceed the design capacity of storm runoff collection systems. In August, 1985 a spill of perchloroethylene into the St. Clair River by Dow Chemical touched off a major investigation into spills as a source of various toxic chemicals in that area. Table 44 shows the frequency of major spills from Ontario sources into the St. Clair River over a ten year period. These spills were all greater than 10 t (approximately 2500

## Table 43

## Compounds, With Accompanying Rationale, Requiring Emphasis in Contaminants Monitoring, Surveillance and Abatement Programs

| GROUP | COMPOUNDS SELECTED | RATIONALE |
|---|---|---|
| I | Hexachlorobenzene<br>Pentachlorophenol | - Persistent Contaminants |
| | Phenanthrene | - PAH (EPA-Priority Pollutant) |
| II | Dichlorobenzene | - highest release levels<br>- & EPA Priority Pollutants |
| III | Chloroform<br>1,1,1-Trichloroethane<br>1,1-Dichloroethylene<br>Tetrachloroethylene | - very high release levels<br>- &<br>- EPA Priority Pollutants |
| | Phenol<br>Xylene | - very high release levels |
| IV | Benzene<br>Toluene<br>Trichloroethylene<br>1,2-Dichloroethane | - high release levels<br>& EPA-Priority Pollutants |
| | Carbon tetrachloride | - EPA Priority Pollutant |
| V | none | - not environmentally significant |
| TOTAL | 18 compounds | |

Source: Craig, 1985

## Table 44

## Spills to St. Clair River or Tributaries

## Involving Ten Tonnes or Greater of Material for Period 1974-1985

| | Year | Source | Spilled (tonnes) | Est. Not Recovered* (tonnes) | Material |
|---|---|---|---|---|---|
| Oil | 1976 | Suncor | 150 | 30 | bunker C |
| | 1976 | Suncor | 300 | 0 | bunker C |
| | 1977 | CNR | 86 | 17 | bunker C |
| | 1978 | Esso Petroleum | 29 | 0 | gas oil |
| | 1980 | Hall Corp. (vessel) | 21 | 13 | bunker C |
| | 1981 | CNR | 21 | 4 | bunker C |
| | 1981 | Esso Petroleum | 348 | 0 | gasoline |
| | 1984 | Esso Petroleum | 116 | 23 | No. 2 |
| | 1984 | Esso Petroleum | 16 | 3 | No. 2 |
| | 1985 | Imperial Bedford (at Shell) | 75 | 1 | cat cracker feed |
| | 1985 | Esso Chemical | 120 | 0 | slop oil |
| | | | ------ | ----- | |
| | | | 1182 | 91 | |
| Latex | 1975 | Polysar | 17 | 17 | |
| | 1976 | Polysar | 18 | 18 | |
| | 1980 | Polysar | 87 | 87 | |
| | 1980 | Polysar | 20 | 20 | |
| | | | ------ | ----- | |
| | | | 142 | 142 | |
| Styrene | 1974 | Dow | 4504 | 2700 | |
| | 1978 | Polysar | 411 | 80 | |
| | | | ------ | ----- | |
| | | | 4915 | 2780 | |
| Inorganic | 1974 | Dow | 21 | 21 | hydrochl. acid |
| | 1975 | Dow | 28 | 28 | sodium hydroxide |
| | 1979 | Dow | 4080 | 4000 | sodium chlorate |
| | 1981 | Polysar | 13 | 13 | sulphuric acid |
| | 1981 | Dow | 379 | 76 | sodium chloride |
| | 1982 | Suncor | 16 | 0 | hydrochl. acid |
| | 1983 | Esso Chemical | 19 | 4 | sodium hydroxide |
| | 1984 | Esso Petroleum | 164 | 33 | brine |
| | | | ------ | ----- | |
| | | | 4720 | 4175 | |
| Miscellaneous | 1975 | Polysar | 159 | 33 | lignin liquor |
| | 1975 | Esso Petroleum | 239 | 239 | phenolic waste water |
| | 1975 | Suncor | 91 | 73 | process water |
| | 1975 | Eagl[illegible]ransport | 11 | 2 | xylene |
| | 1976 | Dow | 13 | 0 | ethylene glycol |
| | 1982 | Esso Petroleum | 46 | 46 | wash water |
| | 1985 | Dow | 54 | 0 | perchloroethylene |
| | | | ------ | ----- | |
| | | | 559 | 393 | |

* Estimate based on reports of percent recovered.

Source: MOE, 1985b

U.S. gallons or equivalent to one quarter of a large tanker). After the oil spills are removed from this list the total amount of toxic chemicals spilled in this area during the ten year period was 10 336 t or 1000 t/a. This value would increase if smaller spills were included. Of these spills 7490 t of special waste were removed. The recovered waste also requires proper handling to prevent further spillage.

Upon investigating the volumes of persistent toxic chemicals spilled into the Great Lakes environment it becomes apparent that spills are a major source. These spills are not related to transportation and occur because the chemicals are not stored securely or are not adequately managed by the industries either using or producing the chemicals.

The number and distribution of PCB spills in 1983 and 1984 in the Great Lakes states is shown in Table 45 (USEPA, 1986). For spill records U.S. data from the Great Lakes basin are relied on. Table 45 also includes an adjustment for unreported spills. According to this current estimate over five tonnes of PCBs are spilled in the Great Lakes states annually. Although analysis of spill records for PCBs is not readily available for Ontario it is most likely that a similar rate but lower amount of spillage has occurred in this province. Much of this spilled waste may be recovered. However this represents one of the major loading sources and exceeds all known sources save for atmospheric

## Table 45

## Distribution of PCB Spill Volumes

### GREAT LAKES STATES

| RANGE (lbs) | NUMBER OF SPILLS | |
|---|---|---|
| UNKN | 14 | |
| 1-3 | 4 | |
| 4-9 | 14 | |
| 10-30 | 33 | |
| 31-99 | 11 | |
| 100-300 | 8 | |
| 301-999 | 4 | |
| 1,000-3,000 | 1 | |
| 3,001-9,999 | 0 | |
| 10,000-30,000 | 0 | |
| 30,001-99,999 | 0 | |
| 100,000+ | 1 | |
| TOT NUMBER | 90 | |
| TOT LBS | 111176 | 50429 kg |
| OUTLIER | 105000 | |
| SAMPLE-OUTLIER | 6176 | |
| MEAN (NO ZEROS) | 1462.8 | |
| MEAN NO OUTLIER | 82.3 | |
| 2-YR WEIGHTED | 45551 | |
| 1-YR WEIGHTED, ADJUSTED FOR UNDER-REPORTING | 113878 lbs | 51654 kg |

Final annual estimate is shown as 51 654 kg of PCBs typically released in accidental spills during any one year.

Source: US EPA, 1986b

deposition (Eisenreich, 1981). Spills of the types mentioned in this section could be reduced in number through treatment of the special waste rather than continued storage.

## 5.7 SOURCES TO THE ATMOSPHERE

The major pathway for most persistent and non persistent environmental contaminants (see chapter 2) is the atmosphere. As it is the major pathway it becomes itself the major source of many compounds (such as PCBs, chlorinated dioxins, and toxaphene) to the Great Lakes. The atmospheric pathway also is the source of the major exposure route of these toxic chemicals to humans, wildlife and fish.

Therefore understanding sources to the atmosphere is critical to reducing toxic chemical exposure. In addition, any management strategies must consider reducing major sources to the atmosphere as well as decreasing major fugitive emissions from many current waste management practices such as land farms and lagoons.

In general many current waste management practices which have been designed, with the best of intentions, to reduce levels of contaminants in aquatic effluents have moved the contaminant sources directly from the water into the atmosphere.

Sanitary landfills continuously emit the gaseous products of anaerobic fermentation along with other volatile materials to the atmosphere. Thus, they can be a continuing source of vapour-phase contaminants to the atmosphere. A recent projection, based on the amount of methane generated annually from landfills and a PCB to methane ratio of 0.3 ug/m$^3$ of $CH_4$ found from landfills sampled, indicates that the annual PCB emissions from sanitary landfills in the US is on the order of 10-100 kg/a. The concentration of PCBs from the incinerator stacks sampled ranged from 0.3 to 3.0 ug/m$^3$ and the annual emissions per stack sampled were 0.25 kg/a. (Murphy et al., 1985)

Other probable sources of atmospheric PCBs include the following: the evaporation of PCBs used in the past for such open uses as paints, wood preservatives, plasticizers, etc; the evaporation of spilled or leaked PCBs from transformers, large capacitors, hydraulic systems and equipment containing large volumes of PCBs and still in service or storage; evaporation from landfills or incinerators of PCBs from materials disposed of in municipal refuse; the evaporation of PCBs improperly disposed of to open areas such as the use of waste PCB fluids to oil roads, etc; emissions of PCBs from engines and furnaces burning liquid or gaseous fuels containing or contaminated with PCBs; the reevaporation of PCBs from land areas where they have been deposited by dry and wet deposition from the atmosphere.

In the past, PCBs were included in the manufacture of a variety of materials that could end up in municipal waste. Some of these materials are still permitted to be disposed of in municipal waste. This includes carbonless copy paper and most of the billions of small, PCB containing capacitors that have been manufactured. Large numbers of these capacitors have been used in the ballasts on fluorescent lighting fixtures, in consumer electronics, and as the starting capacitor on motors in refrigerators, washing machines, air conditioners, etc. There are still no restrictions on the disposal of these capacitors. It has been estimated that, by 1978, 140 million kilograms of PCBs had been disposed of in U.S. landfills (Murphy et al., 1985b).

Volatilization of spills of PCBs and other compounds as mentioned in Chapter 5.3 are also a major source to the atmosphere.

## 5.8 INCINERATION

A growing trend towards incineration of municipal waste and away from landfilling exists in Ontario. There is also an increased requirement for incineration of sewage sludge which has concentrated many industrial organic contaminants (see chapter 5.5), since levels of many contaminants such as PCBs exceed permit requirements for landfilling. Many of the gains made in stopping direct pollution of water via biological treatment plants are lost through the transfer or conversion of special waste which finds its way into sewage sludge into serious atmospheric emissions via improper combustion in municipal incinerators.

The NRC report on chlorinated dioxins (NRC, 1982) estimated the total annual PCDD input to the atmosphere of Ontario from municipal incinerators at 2.2 kg. This was based on the PCDD concentration in precipitated fly ash as determined by Eiceman et al. (1981), the estimated particulate emissions from municipal incineration in the province, and a multiplication factor of 10 times to correct for the PCDD concentration in emitted particulates compared to precipitated fly ash (Lustenhouwer et al. 1980). No attempt was made to estimate nonparticulate, gaseous emissions, nor were any studies conducted to verify the estimated (factored) emission figures.

Since then a number of stack emission tests for PCDD and PCDF have been conducted on two main municipal refuse incinerators (SWARU, Hamilton and Commissioner Street, Toronto) and the largest (Ashbridges Bay, Toronto) of several sewage sludge incinerators in Ontario (Ozvacic et al., 1984). The data from these tests together with the emission parameters documented in the various test runs are shown in Table 46.

The total PCDD and PCDF emissions for the three Ontario sources amount to approximately 8 and 14 kg/a, respectively, for a total PCDD plus PCDF emission of 22 kg/a. In the case of PCDDs, this level (based on three incinerators) is approximately four times higher than the NRC (1982) estimate for all municipal waste incineration sources in Ontario.

In order to put the importance of atmospheric chlorinated dioxins in perspective Table 47 shows that combustion sources clearly exceed all other known environmental sources of chlorinated dioxins. The relative contribution of landfills even from the Niagara River is estimated to be less than 2 to 20 kg/a or 3 to 30 times less than Ontario combustion sources which contribute from 28 to 60 kg of dioxins annually.

## Table 46

### Calculated Annual Emissions of PCDD and PCDF from Two Municipal Waste and One Sewage Sludge Incinerator in Ontario

| Incinerator (date monitored) | Stack Gas Conc. ($ug/m^3$) PCDD | Stack Gas Conc. ($ug/m^3$) PCDF | Stack Flow Rate ($m^3/s$) | Oper'tl Status | Calculated Annual Emissions (g/a) PCDD | Calculated Annual Emissions (g/a) PCDF | Calculated Annual Emissions (g/a) PCDD + PCDF |
|---|---|---|---|---|---|---|---|
| Commissioner St.[a] Toronto | | | | | | | |
| Dec. 1981 | 0.3 | 0.4 | 82.8 | 24 h/d | 682 | 911 | 1593 |
| Dec. 1981 | 1.2 | 1.3 | 80.5 | 7 day/week | 2914 | 3337 | 6251 |
| Dec. 1983 | 1.6 | 1.4 | 86.6 | | 4488 | 3870 | 8358 |
| | | | | Average | 2695 | 2706 | 5401 |
| Ashbridges Bay[b] Toronto | | | | | | | |
| Apr. 1982 | 0.5 | 0.9 | 31.7 | 24 h/d | 482 | 888 | 1370 |
| Apr. 1982 | 1.1 | 0.5 | 31.7 | 7 day/week | 1137 | 500 | 1637 |
| Apr. 1982 | 0.6 | 2.2 | 31.5 | | 589 | 2227 | 2816 |
| | | | | Average | 736 | 1205 | 1941 |
| SWARU[c] Hamilton | | | | | | | |
| May 1982 | 8.6 | 16.3 | 18.3 | 24 h/d | 3555 | 6693 | 10248 |
| May 1982 | 9.7 | 35.6 | 17.2 | 5 day/week | 3736 | 13744 | 17480 |
| June 1982 | 5.8 | 9.1 | 19.0 | | 2467 | 3899 | 6366 |
| | | | | Average | 3253 | 8112 | 11365 |
| SWARU[c] Hamilton | | | | | | | |
| May 1983 | | | | | | | |
| (Ave.) | 2.7 | 6.2 | 16.8 | 24 h/d | 1015 | 2321 | 3336 |
| (Ave. of 13 tests) | | | | | | | |
| (High) | 7.2 | 10.3 | | | | | |
| (Low) | 1.1 | 3.0 | | | | | |

a - annual emissions may overestimate actual output as 3 units were operated during tests; normally only 2 ore operated.

b - annual emissions underestimate actual output as tests were based on a common stack for only 2 units, other unit is older and emits from separate stack when in operation.

c - annual emissions underestimate actual output by a factor of about 2 as tests in 1982 and 1983 reflect monitoring in only 1 of the 2 separate stack flues (boiler #2 in 1982 and boiler 1 in 1983).

Source: MOE, 1985a

Table 47

Summary of Estimated Quantities of PCDDs and PCDFs Entering the Ontario Environment as 2,3,7,8-T4CDD Toxic Equivalents

| SOURCE | | ESTIMATED CURRENT QUANTITY |
|---|---|---|
| 1. | CHEMICAL PRODUCTS<br>(No 2,3,7,8-$T_4$CDD in chemicals in current use) | |
| A. | Penoxy Herbicides (2,4-D, MCPA, dicamba) | 2 - 7 x $10^{-5}$ kg annually |
| B. | Chlorinated Phenols ($P_5$CP, $T_4$CP, $T_3$CP) | 4 kg annually |
| C. | Polychlorinated Biphenyls (PCBs) | 5 kg (not an annual input) |
| D. | Chemical Wastes (A,B, and C) | Unknown |
| E. | Commercial/Domestic Products | Unknown |
| 2. | COMBUSTION | |
| A. | Municipal Refuse/Sewage Sludge | 8 - 10 kg annually |
| B. | All Other Combustion Sources | 20 - 50 kg annually |
| 3. | TRANSBOUNDARY | |
| A. | Airborne | Unknown |
| B. | Waterborne | <2 - 20 kg annually |
| 4. | SEWAGE | Unknown |

Source: MOE, 1985a, p. 4-123

In addition to chlorinated dioxins, combustion sources such as municipal incinerators are also sources of chlorobenzenes, PCBs, and chlorophenols to the atmosphere. Tables 48 and 49 shows that all of these compounds are evident in samples of feedstock going into a municipal incinerator in Hamilton as well as in stack samples of emissions taken from the same incinerator. Similar problems have been found in Virginia and Ohio municipal refuse fired incinerators (Tiernan et al, 1985). The presence of these compounds in high concentrations is logical since these are the precursors to chlorinated dioxins and dibenzofurans. Their presence in the emissions is also indicative of the considerable quantities of contaminants such as PCBs, chlorobenzenes and chlorophenols in the feedstocks of the incinerators particularly in the sewage sludge as shown in section 5.5. Since these compounds are derived, in part, from special waste, better management at the industrial source would reduce the contaminated sewage effluent, the contaminated sludge, and above all the contaminant emissions from municipal incinerators.

A recent Japanese paper went considerably farther in considering not only the fly ash and flue gas emissions from municipal incinerators there but also the extent of contamination of the larger cinders collected (Wakimoto and Tatsukawa, 1985). In this case they found, the same range of concentrations of PCDDs and PCDFs in the cinders as in the fly ash. The volume of the cinders produced amounted to 15 to 30% of the original wastes. Consequently, the largest portion of PCDDs and PCDFs was contained in the cinders not the fly ash. Since cinders

# TABLE 48

## SWARU Incinerator: PCBs, Chlorophenols and Chlorobenzenes in Process Samples (ng/kg)

| | Feedstock | | | Bottom Ash | | | Precipitator Fly Ash | | |
|---|---|---|---|---|---|---|---|---|---|
| Test | CBs | PCBs | ClPh | CBs | PCBs | ClPh | CBs | PCBs | ClPh |
| 1 | 330 | 900 | 12000 | 55 | 100 | 150 | 1000 | 200 | ND |
| 4 | 400 | 500 | 13000 | ND | 25 | ND | 220 | 170 | 12000 |
| 5 | 180 | 40000 | 6400 | ND | 15 | 150 | 120 | 140 | 1300 |
| 6 | 190 | 810 | 7600 | ND | 20 | ND | 120 | 20 | 750 |
| 7 | 2200 | 1500 | 15000 | 10 | 15 | ND | 130 | 45 | 1100 |
| 8 | 480 | 350 | 50 | ND | 10 | 50 | 220 | 110 | 800 |
| 9 | 500 | 320 | 8800 | ND | ND | 150 | 160 | 20 | ND |
| 10 | 210 | 350 | 11000 | ND | ND | 750 | 80 | 45 | 2600 |
| 11 | 460 | 1300 | 32000 | ND | 20 | 300 | 50 | ND | 850 |
| 12 | 480 | 610 | 18000 | 40 | 10 | 250 | 100 | ND | 1300 |
| 13 | 290 | 2500 | 37000 | ND | 15 | 500 | 56 | 50 | 1500 |
| 14 | 1200 | 860 | 100000 | ND | ND | 100 | 150 | 20 | 5000 |
| 15 | 1300 | 1900 | 78000 | ND | 20 | 200 | 310 | 85 | 1000 |

CBs = Chlorobenzenes
PCBs = Polychlorinated biphenyls
ClPh = Chlorophenols

Source: MOE, 1984b

# TABLE 49

## SWARU Incinerator: PCBs, Chlorophenols, and Chlorobenzenes in Stack Samples (ng/m$^3$)

| Test | Chlorobenzenes | PCBs | Chlorophenols |
|---|---|---|---|
| 1 | 110000 | 370 | 85000 |
| 4 | 39000 | 160 | 37000 |
| 5 | 15000 | 630 | 140000 |
| 6 | 62000 | 180 | 74000 |
| 7 | 150000 | 560 | 94000 |
| 8 | 61000 | 170 | 78000 |
| 9 | 120000 | 460 | 190000 |
| 10 | 47000 | 210 | 158000 |
| 11 | 99000 | 4300 | 67000 |
| 12 | 68000 | 1200 | 190000 |
| 13 | 230000 | 2100 | 230000 |
| 14 | 55000 | 450 | 6200 |
| 15 | 46000 | 1200 | 150000 |

Source: MOE, 1984b

are generally landfilled perhaps they too are a form of special waste to be carefully considered for better management in order to reduce environmental impact.

## 5.9 BYPRODUCTS AS SOURCES OF SPECIAL WASTE

A recent U.S. EPA analysis describes the importance of combustion as well as the formation of byproducts or waste in the production of other chemicals. Hexachlorobenzene (HCB) which is found in fish wildlife and humans in Ontario as well as food is an excellent example. Table 50 shows a list of 26 industrial compounds identified as having HCB as a potential byproduct. Recently the USEPA (1986) estimated that up to 858 kg/a of HCB could be produced from municipal and industrial incineration (Table 51). The theoretical importance of chlorobenzenes and chlorophenols formed during the combustion of polyvinyl chloride (PVC) is shown in the schematic (Figure 15). Although HCB has been used as a pesticide, significantly more is derived as a by-product or waste in industrial chemical production, as a byproduct or waste in pesticide production, and from combustion. This compound is similar to chlorinated dioxins and dibenzofurans which are byproducts in chlorophenol production, as well as from combustion. The production is not intentional and it is only by thorough analysis of precursor products and the special waste produced that these compounds can be detected.

## Table 50
## List of 26 Industrial Compounds with Known or Suspect HCB Byproduct

I industrial chemicals (CAS Number) with known HCB byproduct

| | CHEMICAL | SYNTHESIS |
|---|---|---|
| 1. | chlorine (7782-50-5) | NaCl + e |
| 2. | carbon tetrachloride (56-23-5) | $C_1-C_3+Cl_2/450^{\circ}C$ |
| 3. | perchloroethylene (127-18-4) | $C_1-C_3+Cl_2/450^{\circ}C$ |
| 4. | trichloroethylene (79-01-6) | $C_1-C_3+Cl_2/450^{\circ}C$ |
| 5. | pentachlorobenzene (608-93-5) | Benzene+$Cl_2/>200^{\circ}C$ |

II industrial chemicals with potential HCB byproduct

| | | |
|---|---|---|
| a. | chlorinated solvents | |
| 1. | hexachloroethane (67-72-1) | $H_2C=CH_2+Cl_2/140^{\circ}C$ |
| 2. | 1,1,2-trichloro-1,2,2-trifluorethane (76-13-1) | $Cl_2=Cl_2+HF/400^{\circ}C$ |
| 3. | 1,1,2-trichloroethane (79-00-5) | $H_2C=CH_2+Cl_2/120^{\circ}C$ |
| 4. | ethylene dichloride (107-06-2) | $H_2C=CH_2+HCl/300^{\circ}C$ |
| 5. | chlorinated biphenyls (1336-36-3) | biphenyl+$Cl_2/150^{\circ}C$ |
| 6. | chlorinated naphthalene | naphthalene+$Cl_2$ |
| 7. | chlorobenzenes | benzene+$Cl_2/190^{\circ}C$ |
| 8. | dichloropropenes | propylene+$Cl_2/500^{\circ}C$ |
| b. | chlorinated monomers | |
| 1. | vinyl chloride monomer (75-01-4) | $ClCH_2CH_2Cl$+heat |
| 2. | 2-chlorobutadiene (126-99-8) | butadiene+$Cl_2/335^{\circ}C$ |
| c. | chlorinated intermediates | |
| 1. | phosgene (75-44-5) | $CO+Cl_2/200^{\circ}C$ |
| 2. | hexachlorocyclopentadiene (77-47-4) | cyclopentene+$Cl_2$ (335°C) |
| 3. | allyl chloride (107-05-1) | propylene+$Cl_2/510^{\circ}C$ |
| 4. | cyanuric chloride (108-77-0) | Cl-CN/250-480°C |
| 5. | tetrachlorophthalic anhydride(117-08-8) | phthalic anhydride + $Cl_2$ |
| d. | electrolysis chemicals | |
| 1. | sodium metal (7440-23-5) | NaCl + $e^-$ |
| 2. | sodium chlorate (7601-89-0) | NaCl + $e^-$ |
| e. | other chemical production | |
| 1. | titanium dioxide (13463-67-7) | $TiO_2/1000^{\circ}C$ |
| 2. | toluene diisocyanate (26471-62-5) | TDA+ClCOCl/160°C in dichlorobenzene |
| 3. | reactive azo dyes from cyanuric chloride | cyanuric chloride + $RNH_2$ |
| 4. | phthalocyanine dyes and pigments | dye+$Cl_2/200^{\circ}C$ |

Source: USEPA, 1986c

Table 51

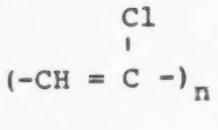
HCB From Municipal and Industrial Incineration

| | | | |
|---|---|---|---|
| A. | WASTE INCINERATED (U.S.) | | 26 x 106 t/a |
| B. | FLYASH GENERATION RATE | | 30 kg/t |
| C. | HCB concentration in flyash | (bottom of range) | 0.01 ug/g |
| | | (top of range) | 1.1 ug/g |
| D. | TOTAL HCB release (A*B*C) | (bottom of range) | 7.8 kg/a |
| | | (top of range) | 858 kg/a |

Source: USEPA, 1986

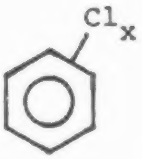
**Figure 15**

**HCB FORMATION DURING MUNICIPAL INCINERATION**

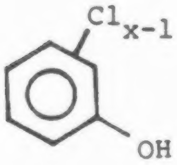


$$(-CH = \overset{\overset{Cl}{|}}{C} -)_n$$

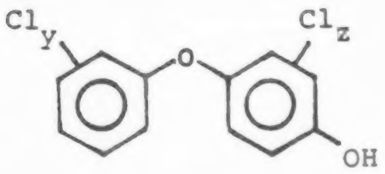
**POLYVINYL CHLORIDE (PVC)**



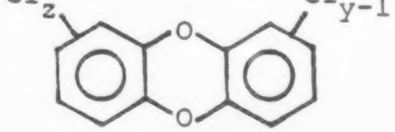
**CHLOROBENZENES**



**CHLOROPHENOLS**



**DIPHENYLETHERS**



**DIOXINS**

## 5.10 ST. CLAIR RIVER POLLUTION INVESTIGATION JANUARY, 1986.

### 5.10.1 INTRODUCTION

One of the best studies of environmental contamination resulting from special waste from Ontario sources is the St. Clair River report (Canada-Ontario, 1985). During the summers of 1984 and 1985 large patches of black oily liquids were found overlying the sediment of the St. Clair River. This prompted a more thorough investigation of contaminants in the bottom sediments of that river. The black oily substance was found to contain high concentrations of many persistent organochlorine chemicals including chlorinated dioxins, 2,4-D, chlorobenzenes and chloroethane. In August 1985, Dow Chemical Canada Inc. of Sarnia accidentally spilled approximately 11 000 L. of perchloroethylene, a toxic dry cleaning solvent into the river. These combined events prompted an immediate investigation of special waste problems along the Ontario petrochemical complex which resides on the St. Clair River.

### 5.10.2 MAJOR FINDINGS OF THE STUDY

The major chemicals present in the St. Clair River were chlorinated organics, such as hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), octachlorostyrene (OCS), pentachlorobenzene, tetrachloro-benzene, trichlorobenzene, carbon tetrachloride and perchloroethylene. These chemicals were found in water, sediment and biota along the Ontario shoreline of the river. The extent of impact was observed as far as the river mouth. There was little transboundary pollution observed from Ontario sources to the Michigan side of the river.

Although there were indications of the definite presence of 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene and carbon tetrachloride in the treated drinking water, there were no violations of the drinking water criteria in the downstream water supplies at Walpole and Wallaceburg.

Surficial sediment results revealed that there were two areas with severe contamination with HCB, HCBD, other chlorinated benzenes and OCS which are major by-products of the production of chlorine and chlorinated solvents manufactured by Dow Chemical. These areas were near the Township ditch which drains the Dow Scott Road landfill site, and in the vicinity of the Dow 1st Street sewer complex. The most significant of these two sources appeared to be Dow's 1st Street sewers. This contamination was a consequence of perchloroethylene liquid losses in conjunction with continuous discharges of the chlorinated organics. Traces of dibenzo dioxins and furans were found but no 2,3,7,8-TCDD or TCDF was detected. It appears that these two areas have a localized effect on the river bottom dwelling organisms. There was a general improvement in the health of the benthic community during the period 1977-1985, with the exception of a section of approximately 100 m along along Dow's shoreline where forms of life were absent. Sediment in this section was acutely toxic. Effects of industrial discharges on the higher food chain (e.g., sport fish) were detected. However, contaminants such as HCB, PCBs, OCS and mercury have declined in sport fish (edible portion) significantly in the last decade.

The St. Clair River Investigation provides a current example of the various types and sources of toxic chemical pollution which occur in Ontario. The types of toxic chemicals released confirm the priority chemicals described in Chapter 2. These are briefly described in the conclusions of the investigation (5.10.3). An analysis of the recommendations (5.10.4) shows the various sources of waste chemicals that occur along the river which require better management.

### 5.10.3 POINT SOURCE SURVEY CONCLUSIONS

The following conclusions were reached by the investigation. These describe the types of priority waste chemicals which were discharged during the study.

1. Dow Chemical effluents, especially the 1st Street sewers, contain many of the same compounds as the perchloroethylene puddles found on the river bottom. The continuous discharge of contaminated effluents from the Dow 1st Street sewers does not in itself account for the formation of the perchloroethylene puddles.

2. Compared with the other point sources sampled, Dow was the major source of neutral extractable chlorinated organics, especially 1,2,4-trichlorobenzene, hexachlorobenzene, hexachloroethane and hexachlorobutadiene.

3. For the Esso Petroleum, Esso Chemical and Sarnia WPCP effluents, the contaminants analysed were generally found at very low concentrations requiring zero or minimal dilutions to achieve ambient water quality standards and objectives. The total net loadings of volatile hydrocarbons from these three sources were 0.96 kg/d, 2.6 kg/d and 2.0 kg/d, respectively.

4. Polysar was a major source of benzene originating mainly in the 1800 mm sewer. The total net loading of volatile hydrocarbons was 115 kg/d of which 112 kg/d was benzene.

5. The Dow sewers are significant sources of volatile pollutants compared with other industrial sources in the present survey and those studied previously on the Great Lakes. The total net loading for volatile hydrocarbons was estimated to be 242 kg/d. Six major pollutants accounted for 84% of this loading (1,2-dichloroethane, perchloroethylene, 1,2-dichloropropane, carbon tetrachloride, benzene and ethyl benzene). Ethylbenzene and benzene totaled 132 kg/d.

6. The Suncor intake, located downstream of Dow Chemicals, contains many of the compounds being discharged at high concentrations by Polysar (benzene only) and Dow. The total net loading of volatile priority pollutants from Suncor was 1.1 kg/d.

7. A comparison of historical organics data for 1979/1980 with the present survey indicates some improvement, but a greater number of samples would be required to make a proper comparison coupled with an examination of abatement measures that have occurred during the period.

8. The Dow Scott Road Landfill leachate contains the chlorophenoxy herbicides 2,4-D (18 ug/L) and 2,4,5-T (1 ug/L), high concentrations of volatile organics including 1,1-dichloroethane, 1,2-dichloroethane, chloroform, trichloroethane and 1,1,2,-trichloroethane. Loadings could not be calculated because of a lack of flow information.

The levels of 2,4-D and 2,4,5-T in the disposal site leachate appeared to be unaffected by carbon treatment as high concentrations of volatiles were also observed after carbon treatment. All chlorophenols were effectively removed by the treatment. The Scott Road site was also a source of trichlorobenzene and hexachlorobutadiene. The Dow 1st Street 750 mm Acid Tile and the Polysar 1700 mm Sewer also contained detectable levels of 2,4-D.

9. The Scott Road Outfall contains many of the contaminants discharged by the Dow Scott Road landfill. However, there may be other sources of chlorinated organics, especially chlorinated benzenes to the Scott Road ditch.

10. The Township ditch water at a point upstream of Polysar is moderately contaminated with volatile organics and extractable chlorinated compounds, specifically: chloroform, 1,2-dichloroethane, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene and hexachlorobutadiene. The loading of volatile hydrocarbons from the Township ditch was similar to that from Polysar. In terms of the loading of chlorinated extractable pollutants, the Township ditch was a greater source of hexachlorobutadiene and trichlorobenzenes than the Dow 1st Street sewers.

11. The Township ditch sediment collected upstream of Polysar is contaminated with chlorinated benzenes, hexachlorobutadiene, octachlorostyrene (found at low levels in most of the samples) and chlorophenols.

12. Urban runoff in the Sarnia area is a minor source of perchloroethylene, hexachloroethane, hexachlorobutadiene, pentachlorobenzene, hexachlorobenzene and octachlorostyrene.

### 5.10.4 RECOMMENDATIONS OF THE STUDY

The following recommendations were made by the investigation team. Section a) describes the toxic chemical problems which require further definition. These are examples of the problems involved with identifying the sources of toxic chemical contamination. Section b) describes the defined sources of the chemical waste. Both the defineable and undefineable environmental sources of waste require better management.

a) Ambient Water Quality

1. The identity and probable sources of sediment contamination that persist in the deeper layers of cores collected in the vicinity of the Ontario shoreline of the river should be investigated.

2. Sources of volatile hydrocarbons particularly carbon tetrachloride and perchloroethylene, in the study area should be investigated and reduced.

3. The apparent increase in concentration of hexachlorobenzene in sediments between the CN tunnel and the Township ditch on the Ontario side should be investigated.

4. The apparent increase in the concentration of hexachlorobenzene in sediments in the vicinity of the CN tunnel on the Michigan side should be investigated.

5. Sources of the carbon tetrachloride and perchloroethylene in water upstream from the CN tunnel should be identified.

6. The presence of high concentrations of mercury in sediments opposite Dow property should be investigated.

7. Sources of hexachlorobenzene, octachlorostyrene, pentachlorobenzene and PCBs in the area between Talford Creek (Shell Canada) and Petrosar should be identified and action initiated to reduce or eliminate these compounds.

8. The drinking water surveillance program should be continued at water treatment plants on the St. Clair River.

9. Ontario drinking water criteria and objectives should be developed for 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene and carbon tetrachloride, all of which have been found in the St. Clair treated drinking water.

10. Contingency drinking water treatment technology should be developed for use after chemical spills, i.e., mobile treatment units.

11. Additional efforts in analytical development should be undertaken to allow more precise analyses of polychlorinated aromatic hydrocarbon and polychlorinated dibenzofurans in young-of-the-year spottail shiners.

12. Additional species of sport fish from Lake St. Clair and Lake Huron (control) should be analyzed for chlorinated benzenes, furans, polyaromatic hydrocarbons and substituted phenols. This is critical requirement, given the importance of the recreational fishery and the high public utilization of fish from Lake St. Clair.

b) Sources

1. The effluent levels of volatile organics, particularly perchloroethylene and carbon tetrachloride from Dow, should be reduced.

2. Based on the findings of water and sediments, Dow effluent levels of persistent chlorinated organics, notably hexachlorobutadiene and hexachlorobenzene, should be reduced.

3. The effectiveness of the Dow Scott Road landfill carbon treatment facility should be investigated. Modifications should be implemented to reduce losses of persistent chlorinated organics, especially hexachlorobenzene and hexachlorobutadiene.

4. Additional sources of chlorinated organics to the Scott Road outfall, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene in particular, should be investigated.

5. Sources of chlorinated organics to the Township ditch, in addition to those coming from the Scott Road outfall, should be investigated.

6. The source of benzene in the Polysar 72-inch sewer and of ethylbenzene and benzene in Dow's sewers should be identified and treated.

7. Volatile hydrocarbons in all sources in the Chemical Valley, particularly carbon tetrachloride and perchloroethylene, should be reduced.

8. To ascertain the extent of possible ground-water contamination in Sarnia area, studies are required to

(i) Define the ground-water flow pattern in the freshwater aquifer.

(ii) Assess water quality in the fresh water aquifer and seepage discharge to the St. Clair River.

(iii) Determine the hydraulic head relationships between the freshwater aquifer, the rock layers above the Detroit River Group, the deep well disposal zone and the caverns in the salina formation.

### 5.10.5 DISCUSSION OF THE ST. CLAIR RIVER REPORT

The types of pollution from Ontario sources evident in the St. Clair River report include direct discharges, spills, discharge from the Sarnia municipal WPCP, leachate from a landfill, and potential seepage from past deep well disposal. The only type of contamination not mentioned was combustion. All of these sources require better management of the special waste involved.

The principal chemical types found are characteristic of the industry, and the St. Clair River sediment. The principal persistent chemicals: chlorobenzenes, chlorostyrenes, chlorophenols and chlorinated dioxins and furans are the basic chemical types found in all Ontario fish, wildlife, and humans as well as food studied to date. These sources in the St. Clair River area are therefore priority sources to reduce.

## 5.11 NIAGARA RIVER TOXIC CHEMICALS COMMITTEE OCTOBER, 1984.

The Niagara River Toxic Chemicals Committee Report (Environ. Can., 1984) is perhaps one of the most well known studies of pollution from special waste since the river is not only infamous but it is close to the population centre of Ontario.

### 5.11.1 PRIORITY CHEMICALS

One of the principal tasks of the Niagara River Toxics Committee was to assess the significance of the types and levels of chemicals found in the Niagara River and its immediate tributaries.

Chemicals were placed in lists according to priority. Table 52 lists the most problematic chemicals found in the Niagara River.

### 5.11.2 ONTARIO DISCHARGES OF PRIORITY CHEMICALS TO THE NIAGARA RIVER

Although the Niagara River report points out the major contribution of US sources to the toxic chemical loading of the river and the US landfills there are known worldwide, Ontario also contributes to the problem. Some Ontario sources of special waste were highlighted under section 5.2. However this section will deal with the area more comprehensively.

The following were the major Ontario sources and significant types of special waste discharged to the Niagara River when the report was compiled.

## Table 52

## Chemicals of Concern Found in the Niagara River.

Adrin
Aniline
Antimony
Arsenic
Benzene
Benzofluroanthene
Benzoanthracene
Benzpyrene
Berylium
BHC-
Bis phthalate
Bromoform
Cadmium
Carbon tetrachloride
Chlordane
Chlorodibromomethane
Chloroform
Chloronaphthalene
Chromium
Chrysene
Copper
Cyanide
2,4-D
DDD
DDE
DDT
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichloroethane
1,2-Dichloroethylene
Dichlorobromomethane
Dichloronaphthalene
Dieldrin
Dioctyl phthalate
Diphenylamine
Endosulphan
Endrin
Ethylbenzene
Flouranthene
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Lead
Lindane
Mercury
Methoxyclor
Methylene chloride
Mirex
Nickel
Pentachlorobiphenyl
Pentachlorophenol
Phenol
Polychlorinated Biphenyl-Arochlor 1242
Polychlorinated Biphenyl-Arochlor 1254
Polychlorinated Biphenyl-Arochlor 1260
Pyrene
Selenium
Silver
Styrene
2,4,5-T
TCDD
Tetrachlorobiphenyl
Tetrachloroethene
Tribromomethane
Trichloroethene
Trichloronaphthalene
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol
Trichlorophenol
Zinc

### Fort Erie (Anger Ave.) WPCP

The Fort Erie WPCP is a primary treatment facility.

| Parameter | kg/d | lbs/d |
|---|---|---|
| Phenols | 0.27 | 0.60 |
| Copper | 0.49 | 1.08 |
| Zinc | 1.30 | 2.86 |
| 1,2-Dichloroethane | 0.32 | 0.70 |
| Trans-1,2-Dichloroethylene | 1.79 | 3.94 |
| Dimethyl phthalate | 0.75 | 1.65 |
| Dibutyl phthalate | 0.99 | 2.18 |

### Fleet Manufacturing

Fleet manufactures aircraft, satellite, and radar equipment and components. The effluent does not comply with the MOE discharge objectives for chromium (1 mg/L), producing an estimated load of 1.08 kg/d (2.38 lbs/d).

### Atlas Steels

The following chemicals were of concern in the Atlas Steels final effluent:

| Parameter | kg/d | lbs/d |
|---|---|---|
| Chromium | 32.64 | 71.96 |
| Copper | 1.36 | 3.00 |
| Lead | 4.62 | 10.19 |
| Nickel | 27.2 | 59.98 |
| Zinc | 4.35 | 9.59 |
| Trichloroethylene | 3.04 | 6.70 |

It was anticipated that recent measures, ie. the North Plant treatment facility and the new solidification plant (for the treatment of spent acids and alkalis, and pickling rinse waters), would reduce the average discharge loadings of metals.

## Cyanamid at Niagara Falls

Cyanamid at Niagara Falls manufactures calcium carbide, cyanide and cyanamide.

| Parameter | kg/d | lbs/d |
|---|---|---|
| Zinc | 0.60 | 1.32 |
| Cyanides | 0.96 | 2.11 |
| Butylbenzyl phthalate | 0.35 | 0.77 |

## Cyanamid Welland Plant

The Cyanamid Welland Plant manufactures nitrogen and phosphorus fertilizers, nitric acid, HDS catalyst, and dicyanamide.

| Parameter | kg/d | lbs/d |
|---|---|---|
| Chromium | 4.87 | 10.7 |
| Nickel | 2.34 | 5.15 |
| Zinc | 2.04 | 4.49 |
| Copper | 0.65 | 1.43 |
| Cyanides | 2.29 | 5.04 |

## Niagara Falls WPCP

The Niagara Falls WPCP provides primary treatment and phosphorus removal with a rated capacity of 58200 $m^3/d$ (15.3 mgd). Upgrading to secondary treatment has been proposed and is in the planning stage.

| Parameter | kg/d | lbs/d |
|---|---|---|
| Phenols (4AAP) | 0.87 | 1.91 |
| Chromium | 3.57 | 7.85 |
| Copper | 0.93 | 2.05 |
| Lead | 0.57 | 1.25 |
| Zinc | 11.3 | 24.9 |
| Methylene chloride | 0.39 | 0.86 |
| Cyanides | 0.34 | 0.75 |

| | | |
|---|---|---|
| 2,4-Dichlorophenol | 0.39 | 0.86 |
| Dibutyl phthalate | 3.40 | 7.48 |
| Diethyl phthalate | 0.79 | 1.74 |
| Bis(2-ethylhexyl) phthalate | 0.30 | 0.66 |

Welland Water Pollution Control Plant (WPCP)

The Welland WPCP provides secondary treatment (conventional activated sludge) and phosphorus removal and had a design capacity in 1981 of 45400 $m^3$/d. The plant has since been expanded to 68100 $m^3$/d.

| Parameter | kg/d | lbs/d |
|---|---|---|
| Copper | 0.70 | 1.54 |
| Lead | 13.4 | 29.4 |
| Zinc | 1.71 | 3.76 |

McMaster Ave. Combined Sewer

The McMaster Ave. Combined Sewer contains industrial and sanitary wastewater, industrial cooling water, and storm water. Since the time of the surveys, some storm water and industrial cooling water have been segregated; however, sanitary and industrial wastewater continue to be directed to the Welland River.

| Parameter | kg/d | lbs/d |
|---|---|---|
| Phenols (4AAP) | 0.37 | 0.81 |
| Chromium | 2.2 | 4.84 |
| Copper | 1.01 | 2.22 |
| Lead | 4.64 | 10.2 |
| Nickel | 3.56 | 7.83 |
| Zinc | 1.37 | 3.01 |
| Di-n-butyl phthalate | 0.26 | 0.57 |
| Bis(2-ethylhexyl) phthalate | 0.27 | 0.58 |

Ontario Urban Runoff

Table 53 shows the estimated loading of toxic substances in urban runoff to the Niagara River on an annual basis.

The highest annual loadings were computed for metals, which totalled over 16 t/a (lead-5.9 t/a, zinc-6.2 t/a, chromium-1.8 t/a, nickel-1.0 t/a, and copper-1.1 t/a). Other loadings were 22 kg/a of polycyclic aromatic hydrocarbons, 10 kg/a of chlorinated benzenes, 2 kg/a of PCBs, and 1.5 kg/a of organochlorine pesticides (Marsalek, 1983).

Ontario Landfills

Seventeen landfill sites have been identified in the Niagara and Welland River drainage basins in Ontario. Of these, five have been identified as having a significant potential to contaminate the Niagara River. Of these sites, it was the Committee's opinion that the Atlas Steels landfill was contributing contaminants to the Niagara River via the Welland River.

### 5.11.3 DISCUSSION OF THE SPECIAL WASTE PROBLEMS ON THE NIAGARA RIVER AS THEY RELATE TO THE OVERALL ONTARIO PROBLEM

The major Ontario special waste problems on the Niagara River relate more to metal contamination than organic chemicals. This is in direct contrast to the St. Clair River where organic chemicals predominated. However, analytical methods and protocols focused on organics on the St. Clair and metals on the Niagara perhaps creating on artificial discrepancy. Recovery systems for these metals when installed will create a requirement

## Table 53

## Annual Total Loadings of Toxic Substances in Urban Runoff to The Niagara River From The Urban Study Area (kg/a)

| Substances | Annual Total Loadings in Water and Sediment | | |
|---|---|---|---|
| | Lower Estimate | Upper Estimate | Best Estimate |
| PCBs | | | |
| Total polychlorinated biphenyls | 0.56 | 4.2 | 2.1 |
| Organochlorine Pesticides | | | |
| Hexachlorobenzene | 0.0093 | 0.060 | 0.027 |
| alpha - BHC | 0.25 | 0.44 | 0.34 |
| Lindane | 0.093 | 0.21 | 0.14 |
| Heptachlor | 0.0022 | 0.047 | 0.017 |
| Aldrin | 0.0002 | 0.040 | 0.011 |
| Heptachlor epoxide | 0.011 | 0.055 | 0.025 |
| gamma-Chlordane | 0.050 | 0.46 | 0.021 |
| alpha-Chlordane | 0.069 | 0.66 | 0.29 |
| alpha-Endosulphan | 0.0060 | 0.065 | 0.025 |
| p,p'-DDE | 0.016 | 0.16 | 0.073 |
| Dieldrin | 0.0032 | 0.064 | 0.023 |
| Endrin | 0.097 | 0.11 | 0.042 |
| o,p'-DDT | 0.0052 | 0.096 | 0.034 |
| p,p'-TDE | 0.012 | 0.087 | 0.034 |
| p,p'-DDT | 0.017 | 0.19 | 0.080 |
| beta-Endosulphan | 0.017 | 0.082 | 0.036 |
| Mirex | 0.0013 | 0.066 | 0.029 |
| Methoxychlor | 0.016 | 0.13 | 0.056 |
| Polyaromatic Hydrocarbons | | | |
| Indene | 0.0031 | 1.8 | 0.68 |
| 1,2,3,4-Tetrahydro-naphthalene | 0.0031 | 1.8 | 0.68 |
| 2-Methylnaphthalene | | | |
| Quinoline | 0.13 | 1.8 | 0.74 |
| 1-Methylnaphthalene | 0.015 | 1.8 | 0.68 |
| beta-Chloronaphthalene | 0.056 | 1.8 | 0.70 |
| Acenaphthylene | 0.11 | 1.8 | 0.74 |
| Acenaphthene | 0.23 | 2.0 | 0.88 |
| Fluorene | 0.0062 | 1.8 | 0.67 |
| Phenanthrene | 0.69 | 7.2 | 3.2 |
| Fluoranthene | 1.1 | 9.4 | 4.3 |
| Pyrene | 3.7 | 34 | 15 |

Table 53 (con't)

Annual Total Loadings of Toxic Substances in Urban Runoff To The Niagara River From The Urban Study Area
(kg/a)

| Substances | Annual Total Loadings in Water and Sediment | | |
|---|---|---|---|
| | Lower Estimate | Upper Estimate | Best Estimate |
| **Chlorinated Benzenes** | | | |
| 1,3-Dichlorobenzene | 0.057 | 0.82 | 0.26 |
| 1,4-Dichlorobenzene | 0.11 | 1.2 | 0.47 |
| 1,2-Dichlorobenzene | 1.01 | 4.6 | 2.4 |
| 1,3,5-Trichlorobenzene | 1.5 | 14 | 6.2 |
| 1,2,4-Trichlorobenzene | 0.036 | 0.23 | 0.11 |
| 1,2,3-Trichlorobenzene | 0.051 | 0.051 | 0.22 |
| 1,2,4,5- + 1,2,3,5-Tetrachlorobenzene | 0.0067 | 0.12 | 0.041 |
| 1,2,3,4-Tetrachlorobenzene | 0.0017 | 0.092 | 0.029 |
| Pentachlorobenzene | 0.0009 | 0.089 | 0.029 |
| Hexachlorobenzene | 0.0064 | 0.055 | 0.022 |
| **Trace Elements** | | | |
| Arsenic | 28 | 150 | 76 |
| Cadmium | 8 | 33 | 18 |
| Copper | 390 | 2100 | 1100 |
| Cobalt | 30 | 210 | 96 |
| Chromium | 450 | 4000 | 1800 |
| Lead | 1500 | 13000 | 5900 |
| Mercury | 100 | 150 | 130 |
| Nickel | 320 | 2000 | 990 |
| Selenium | 20 | 31 | 27 |
| Zinc | 2200 | 12000 | 6100 |

Source: Marsalek, 1983.

for proper disposal, treatment, or recycling of the residue. It is interesting to note that although the direct industrial discharge relates to metals, organic chemicals are prevalent in urban runoff and in municipal treatment plant effluents. Industrial landfills are also a problem on the Niagara River as well as the St. Clair River.

It is emphasized throughout the NRTC report that Ontario accounts for about 10% of the problem on that river. That Ontario problem is generally the same type of problem as occurs on the U.S. side of the river although smaller in magnitude relative to the extent of industrialization on the Ontario side. Table 54 shows that of the ten international major contributing sources, four are municipal treatment plants contaminated with industrial waste; two are steel companies and one a large related coke company; two are chemical companies; and one is a power corporation. Table 52 on priority chemicals in the Niagara River although longer contains the chemicals found in the St. Clair River and the chemicals found in Ontario fish, wildlife, humans and food.

The types and sources of the international special waste problems are similar to those in Ontario, ie. municipal treatment plants, key industrial discharges and old landfills. U.S. sources are larger in magnitude because of the greater U.S. industrial base in New York State. However, Ontario has the same types and sources of special waste problems to manage as those in the U.S.

## Table 54

### Ten Most Significant Point Sources of EPA Priority Pollutants to the Niagara River

| Facility | Loading kg/d |
|---|---|
| 1. Buffalo Sewer Authority WWTP, N.Y. | 438 |
| 2. Niagara Falls, N.Y. WWTP | 190 |
| 3. Bethlehem Steel Corp., N.Y. | 178 |
| 4. Niagara Mohawk Power Corp., N.Y. | 155 |
| 5. Atlas Steels, Ontario | 73.7 |
| 6. Olin Corp., N.Y. | 55.1 |
| 7. Spaulding Fibre Co. N.Y. | 35.7 |
| 8. Town of Tonawanda WWTP, N.Y. | 26.8 |
| 9. Town of Amherst WWTP, N.Y. | 25.6 |
| 10. Donner-Hanna Coke Joint Venture, N.Y. | 25.2 |
| Total | 1203.1 |

Source: Environ. Can., 1984.

## 5.12 MAJOR FINDINGS

a) The two general sources of residues derived from special waste entering the Ontario environment are industrial discharges from many sectors and municipal treatment plants which are contaminated with industrial waste.

b) Current incineration practices, particularly for sewage sludge and municipal refuse contaminated with industrial residues add to the contamination problem caused by either the dispersion of the industrial residues through the atmosphere, or via the creation of more highly toxic byproducts such as chlorobenzenes, chlorinated dioxins and chlorinated dibenzofurans.

c) Alternately, if the industrial special waste entering municipal treatment systems were removed and treated at the source the emissions and discharges mentioned above in both a and b would be greatly reduced.

d) The primary persistent organic contaminants coming from Ontario industrial discharges, particularly in the St. Clair River area and international discharges in the Niagara River area, are found as contaminants in Ontario wildlife, fish, humans and food. These residues include PCBs, chlorobenzenes, chlorostyrenes, chlorinated dioxins and dibenzofurans, chlorophenols, and polynuclear aromatic hydrocarbons.

e) Industrial spills and accidental discharges are currently a major source of contaminants to the environment which could be controlled by better management. Chemicals and special waste which have been recovered from spills also require better means of treatment so that they will not become a future problem.

f) Leachate from old landfills and seepage from deepwell disposal practices are also environmental sources of residues derived from special waste in Ontario. Problems are evident on the St. Clair River and Niagara River. Ontario has classified 69 active waste sites, and 99 closed waste sites that have received industrial liquid or hazardous waste as a concern due to potential impact on human health (MOE, 1986). Their contents or at minimum the leachate collected from these facilities may well be considered a significant source of special waste to the Ontario environment.

g) Ontario data on sources of special waste in the environment are very limited particularly for organic contaminants. Major loadings of persistent contaminants requiring better management are documented as coming from iron and steel mills, pulp and paper mills, refineries, petrochemical industries, and municipal treatment plants.

# CHAPTER 6

# REVIEW OF MAJOR ENVIRONMENTAL AND POLICY DOCUMENTS RELATING TO SPECIAL WASTE PROBLEMS

## 6.1 INTRODUCTION

Toxic chemicals in the environment and human health problems associated with toxic chemicals have been the subject of many reviews by the federal and provincial governments, international bodies such as the International Joint Commission on Great Lakes Water Quality, and impartial non-governmental scientific bodies such as the U.S. National Academy of Science and Royal Society of Canada. This chapter looks at the need for management of special waste problems as seen through the eyes of:

6.2) The I.J.C. Great Lakes Water Quality Board, Report published in June 1985,

6.3) The I.J.C. Human Health Effects Committee on Toxic Chemicals found in the Great Lakes basin,

6.4) The 1985 review of the Great Lakes Water Quality Agreement by the U.S. National Academy of Science and Royal Society of Canada, and 6.5) The 1986 World Conference on Toxic Chemicals in Large Lakes which was hosted by the Governor of Michigan.

These documents are reviewed to examine common problems associated with special waste management and the recommendations of the diverse groups are presented regarding the need for special waste management along with some recommendations as to how and when to do it.

## 6.2 1985 REPORT BY THE INTERNATIONAL JOINT COMMISSION GREAT LAKES WATER QUALITY BOARD

The Great Lakes Water Quality Board audits the problems and programs implemented by governments to meet the objectives of the Great Lakes Water Quality Agreement. The following are a series of excerpts from the 1985 report regarding toxic chemical problems in the Great Lakes Basin area (IJC, 1985b).

### 6.2.1 SOURCES AND PATHWAYS

> Many anthropogenic substances enter the ecosystem by pathways and in concentrations which do not easily lend themselves to control. Major pathways include not only municipal and industrial point sources but also urban storm water discharges and combined sewer overflows; rural land runoff; atmospheric deposition; groundwater migration, including pollutants coming from waste disposal sites and landfills; and release from bottom sediment in rivers and simply do not lend themselves to normal pollution control technology. Indeed, there are questions as to whether some of these sources can be controlled in any economically acceptable fashion.

### 6.2.1.1 MUNICIPAL AND INDUSTRIAL POINT SOURCES

The best quantified and historically the largest source of persistent toxic substances to the Great Lakes system are industrial and municipal point sources. These sources are regulated through established programs in both countries. Experience has shown that municipal and industrial discharges are the most controllable sources.

### 6.2.1.2 STORM WATER DISCHARGES AND COMBINED SEWER OVERFLOWS

Storm water discharges and combined sewer overflows are known sources of persistent toxic substances; their impact has been clearly documented in localized situations, such as harbours. However, the overall magnitude of these sources and their impact on the open lakes is unclear. In some well documented problem areas, such as Milwaukee, structural solutions are being implemented.

### 6.2.1.3 ATMOSPHERIC CONTAMINATION

Believed to be a significant pathway, atmospheric deposition of persistent toxic substances to the lakes is considered to be poorly understood and quantified. The volatilization process of these chemicals from the water column to the air is also not fully understood.

Authority to regulate emissions to the atmosphere is based on clean air requirements. However, since atmospheric deposition is suspected to be a significant pathway by which persistent toxic substances reach the Great Lakes, additional authority and effort may be required to control emissions, with the specific added goal of protecting the Great Lakes ecosystem.

### 6.2.1.4 GROUNDWATER CONTAMINATION

Waste disposal sites and deep well disposal have been documented as real and potential sources of contamination to groundwater. The groundwater, which is a major source of water to the lake system, can transport these contaminants to the surface waters. Based on studies conducted under the auspices of the Niagara River Toxics Committee, plus other site-specific studies, it is suspected that groundwater contribution of persistent toxic substances is substantial. However, considerable work is needed before the magnitude and significance of the total contribution is understood.

#### 6.2.1.5 AGRICULTURAL ACTIVITIES

The surface runoff of persistent agricultural pesticides from farm lands into the Great Lakes has been a historic concern. It has not, however, been well quantified. Both Canada and the United States have banned the use and production of certain agricultural chemicals, such as toxaphene and DDT.

No till, ridge till, and other agricultural practices, are presently being promoted to reduce soil erosion and phosphorus and pesticide runoff into surface waters. These practices have resulted in expanded use of chemicals to control weeds and pests. With reduced surface runoff and expanded use of chemicals, the concern is now the increased quantity of pesticides entering the groundwater via percolation through the soil. The long-term system implications for the lakes need to be understood.

#### 6.2.1.6 IN-PLACE POLLUTANTS

The historic deposition of persistent toxic substances into sediments has been singled out as the major concern in many localized situations. These sediments can be a source of pollutants into and through the food chain. Activities to remove, treat, isolate, or dispose of polluted sediments are underway or proposed in some areas. The impacts of the removal and disposal technologies being considered need to be carefully monitored and refined.

### 6.2.2 CRITICAL POLLUTANTS

By consensus, the Water Quality Board has developed the following list of Critical Pollutants:

Total polychlorinated biphenyl (PCB)
Mirex
Hexachlorobenzene
Dieldrin
DDT and metabolites
2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)
2,3,7,8-tetrachlorodibenzofuran
Benzo-a-pyrene
Alkylated lead
Toxaphene
Mercury

These chemicals are all present in the Great Lakes ecosystem (some locally, some widespread), are highly toxic, persistent, and can bioaccumulate to levels which can threaten human health and the aquatic ecosystem. The concern regarding these substances is not new, nor are control programs for some of these substances; their presence and detrimental effects have been recognized for years.

The Board considers it reasonable to use these selected substances to characterize sources and pathways and to guide surveillance, modelling, and remedial studies. Several of these chemicals are members of larger families, so that a control action taken for one substance would concurrently control other substances as well.

### 6.2.3 AREAS OF CONCERN IN THE GREAT LAKES BASIN

The Board has described 42 areas of concern, of which 15 are in Ontario. These Ontario areas are described in Appendix A. In 13 of these 15 areas of concern in Ontario, surveillance and monitoring have found concentrations of one or more toxic substances. The 15 areas of concern are Peninsula Harbour, Jackfish Bay, Nipigon Bay, Thunder Bay, Collingwood, Penetang Bay to Sturgeon Bay, the Spanish River, Wheatly Harbour, the Bay of Quinte, Port Hope, the Toronto Waterfront, Hamilton Harbour, the St. Mary's River, the St. Clair River, and the Detroit River. Other than Penetang, and the Bay of Quinte, all have listed toxic chemical problems associated with past or current discharge of chemicals derived from special waste. In some areas the reported levels only exceed objectives/guidelines on a periodic rather than a chronic basis; this suggests improving conditions.

Fish consumption advisories for the protection of human health are in effect in many of the areas of concern. Fish consumption advisories generally apply to large parts of a lake or channel and the source of the contaminant may not necessarily be associated with the local area. Fish consumption advisories have been issued primarily because of contamination by PCBs and/or mercury. Municipal and industrial discharges have historically been the major source of pollutant inputs to the Great Lakes. Consequently, the emphasis of the 1972 Agreement was the implementation of remedial programs to abate these sources. These programs have been effective in reducing loadings of both conventional pollutants (e.g. nutrients, bacteria, and oxygen-consuming materials) and to some extent toxic substances (e.g. heavy metals, certain organics, and phenols). Most point sources are generally in compliance with their current discharge effluent requirements. Such measures will continue to reduce the pollutant loadings in these areas. It is expected that all major municipal discharges will have implemented measures adequate for the control of conventional pollutants by the late 1980s.

## 6.3 REPORT OF THE COMMITTEE FOR THE ASSESSMENT OF HUMAN HEALTH EFFECTS OF GREAT LAKES WATER QUALITY 1981 AND 1986

The first task of the Human Health Effects Committee was to consider available data on acute or chronic toxicity, neurotoxicity, reproductive effects, carcinogenicity, and teratogenicity in the evaluation of the health hazard of each chemical listed in Appendix E of the Water Quality Board's 1977 Report on Great Lakes Water Quality. This list of about 300 chemicals found in the Great Lakes at that time was used in formulating the 1978 Great Lakes Water Quality Agreement. In 1981 the committee published the first assessment report on 91 chemicals. In 1986 a second report was published updating this report. The full analysis of these chemicals is summarized in Appendix B. The 18 chemicals which are a human health concern were determined from exposure from drinking water or via fish (Table 54). Thirteen of the chemicals of concern to human health are derived from special waste.

## 6.4 REVIEW OF THE GREAT LAKES WATER QUALITY AGREEMENT BY THE U.S. NATIONAL ACADEMY OF SCIENCE AND THE ROYAL SOCIETY OF CANADA. DECEMBER, 1985.

The 1978 Great Lakes Water Quality Agreement was reviewed by a joint committee (U.S. National Academy of Science and Royal

## Table 54

## Compounds Found in the Great Lakes Considered to be at a Level of Concern for Human Health

| | |
|---|---|
| Pesticides | Alachlor |
| | Oxychlordane |
| | Hexachlorobenzene |
| | Pentachlorophenol |
| | 2,4,5-Trichlorophenol |
| Compounds Derived From Special Waste | Hexachlorobenzene |
| | Pentachlorophenol |
| | Carbon tetrachloride |
| | 1,2-dichloroethane |
| | Trichloroethene (trichloroethylene) |
| | Tetrachloroethene (tetrachloroethylene) |
| | Hexachlorobutadiene |
| | Alpha-hexachlorocyclohexane |
| | 2,4,6-trichlorophenol |
| | 2,4,5-trichlorophenol |
| | 1,4-dioxane |
| | Diethylhexyl phthalate (DEHP) |
| | Chlorinated dioxins and dibenzofurans |

Source: I.J.C. 1985a

Society of Canada), in 1985. The following covers the committee's recommendations (6.4.2) pertaining to toxic chemicals in the Great Lakes Basin covering the need and requirements for better management of toxic waste. The committee's discussion of a toxic chemical management strategy (6.4.3) is also included because of its relevance to this report.

## 6.4.1 INTRODUCTION

> The evidence of continuing high levels of toxic contaminants in the Great Lakes, and the complexity of controlling the diverse sources of these substances, lead the committee to conclude that the current programs for controlling persistent toxic substances in the Great Lakes ecosystem are inadequate. Because of the diverse sources of substances (air, land, groundwater, and industrial sources), the lipophilic character of many of the chemicals such as PCBs and dioxins, the hydrologic residence times of the lakes, the ability of the chemicals to biomagnify in the food chains, the evidence of effects on the ecosystem and subtle effects on humans exposed to the chemicals, the lack of effective control holds the risk of serious effects for generations to come (NAS/RSC, 1985).
>
> The committee found substantial evidence that the human population living in the Great Lakes basin is exposed to, and accumulates, appreciably more toxic chemical burden than people in other similarly large regions of North America for which data are available. The difference appears to be largely due to the higher contaminant levels in food products derived from the Lakes and their basin.
>
> Thus, the committee concluded there is an urgency for approaches having the potential to achieve reduction of toxic pollutants in the Great Lakes and in the human population of the basin at the earliest possible date. Current research is exploring further the intricacies of potential effects, and experience indicates that the consequences may be found to be even more severe than currently recognized. At the same time, there is evidence that the pollution of the Great Lakes is having some negative effect on economic development (NAS/RSC, 1985).

Significant economic cost may be incurred through increased human morbidity and mortality and anguish about health risks; adverse effects on agricultural productivity; and decreased use of the resources of the Great Lakes. It is conceivable that further insult to the already degraded Great Lakes basin ecosystem may result in tremendous costs. The health and cleanup costs to future generations may be substantially greater than they are to the present generation in that the toxic substances may have become distributed more widely. Without a sustainable ecosystem, it is difficult to envision a sustainable economy in the long term.

### 6.4.2 RECOMMENDATIONS OF THE COMMITTEE

The joint review provided the following definitive recommendations on the need and requirements for better hazardous waste management (NAS/RSC, 1985).

a) The committee recommends that measures be taken to increase the awareness of the public (including industry and politicians) as to the extent and implications of the toxic chemicals problems in the Great Lakes basin.

b) The committee recommends that the Agreement encourage action on the major sources of contamination at the areas of concern, that effective solutions be implemented, and that rigorous evaluative case studies be undertaken and published.

c) The committee strongly recommends that as part of a comprehensive toxic substances management strategy there should be components that deal fully with the diverse sources of contamination. This will require:

- An inventory of all sources of toxic chemicals found at potentially significant levels in the Great Lakes ecosystem and, within the limits of data availability, those that are not responding to present control actions. This inventory would include extrabasin and intrabasin gaseous and particulate emissions, land-based inputs, resuspension from sediments, and inputs from contaminated groundwater.

- Actions toward an effective long-term solution to leaking toxic waste dumps recognizing that although expensive in the short run, the result can be expected to be of benefit to the health of the Great Lakes ecosystem and human population.

- Control actions against all identifiable sources of toxic chemicals to the Great Lakes basin. Studies on the cost-effectiveness of action programs should include the long-term benefits of such programs.
- Siting and operation of modern toxic-waste treatment centers in all regions of the basin. An annex should be added to the Agreement to provide for strict management of toxic wastes, both those disposed of carelessly in the past and those in prospect for the future.

### 6.4.3 TOXIC CHEMICAL MANAGEMENT STRATEGY

The report of the joint committee which reviewed the Great Lakes problem (NAS/RSC, 1985) emphasized prevention of exposure to toxic chemicals and the need for better hazardous waste management. The following toxic chemical management strategy is excerpted directly from the report of the committee.

> Dealing effectively with chemical contamination problems within the Great Lakes basin necessitates considering the whole life cycle of hazardous chemicals, including production, usage, and disposal, as well as inputs from long-range transport. The use and dispersal of chemicals in the Great Lakes basin is widespread. Pesticides in agriculture account for an average annual release of 10 kilograms of chemicals per hectare in the environment; household consumption of pesticides, solvents, and chemicals is well over 20 kilograms per hectare. The latter, and chemicals from many other diffuse sources find their way into the sewer systems, directly or as a result of runoff. An ecosystem approach requires a substantial effort to address the prevention side as well as the remediation side of the toxic chemicals problem.
>
> Because of the long retention times of persistent toxic chemicals in the lakes, controls should be based on a load allocation plan using a mass balance concept rather than effluent concentrations. Such a plan has been suggested for the Niagara River in the Niagara River Toxics Committee Report, October 1984 (Report of the Niagara River Toxics Committee, 1984). This type of plan would progressively decrease ceilings on loading levels with an ultimate goal of zero discharge as described in Annex 12 of the Great Lakes Water Quality Agreement. Target loads for toxic substances would be developed similar to the target loadings for phosphorus in the supplement to Annex 3 of the Agreement. Development of the models supporting this type of allocation are found in papers by Rogers and Swain (1983) and Hallett (1985).

Modern toxic waste treatment technology is highly reliable, as compared with dumping the waste in landfills. High-temperature incinerators can destroy more than 99.99 percent of organic toxic materials; solidification processes neutralize inorganic waste and cast it into a cement-like solid; special technologies such as incineration in high-temperature plasma and the scrubbing of effluents in molten salt beds can be used to destroy safely more refractory organic materials. Yet, releasing 0.01 percent of large quantities of toxic chemicals, the nature of which is unknown, contributes to atmospheric pollution and attracts the attention of the public, though the overall benefits of a reduction of 99.99 percent would obviously be great.

The prevention side of the toxic chemicals problem requires the banning of particularly hazardous chemicals, replacement of persistent toxic chemicals by less persistent, less-toxic alternatives, and the encouragement of the public and industries to recycle waste materials to the greatest extent possible. Education of the general public about the extent of the problem and the encouragement of a conservation ethic for society are important aspects of a comprehensive program for the management of toxic chemicals. Because hazardous chemicals may endanger human health and be injurious to resources basic for the economy, industry and consumers must, in cooperation with government institutions, work toward the establishment of an efficient hazardous chemical control strategy. The following principles are presented as guidelines for this control strategy:

(a) The replacement of the hazardous chemicals used in agriculture, forestry, and households by less-harmful alternatives. Study and education should focus on the most cost-effective benefit using the minimal amount of a chemical, e.g., integrated pest management for agriculture, forestry, and fisheries.

(b) The reduction of hazardous emissions should become a priority objective of the plant modernization process, with a longer-term goal of zero discharge. This includes the development of closed-loop systems and the use of nonhazardous nonpersistent alternatives.

(c) The establishment of effective hazardous-waste treatment facilities is necessary to ensure that risks to human health are eliminated to the greatest extent possible. Treatment facilities and programs should become precious assets of economic development and valuable contributors to solving problems of national interest.

(d) There is a need for cooperation between regulatory agencies and resource departments in fostering innovation in waste-treatment technology by streamlining environmental requirements and offering financial incentives.

(e) Basin municipalities and their citizens should make commitments to purify potable water with even traces of organic contaminants. This includes research into alternative treatments for drinking water, e.g., filtration through granular activated carbon.

(f) The determination of mass balances of the chemicals in circulation within the Great Lakes basin ecosystem is an essential feature of a chemical control strategy that interrelates all the above.

## 6.5 WORLD CONFERENCE ON LARGE LAKES

This conference was hosted by the Governor of Michigan in May, 1986 and brought scientists, politicians and industrial leaders from 41 countries together. It was focused entirely on toxic chemical problems. Four separate themes were followed dealing with effects, sources and fate, fisheries, and socio-economic and political areas.

Several key recommendations from each of these different orientations coincide. First is the need to provide the public with clear, concise, and accurate data regarding the health of the ecosystem. Second is the call for a preventive approach to the management of toxic substances and the immediate need to stop the sources of persistent toxic chemicals. Finally is the requirement to document human exposure and chronic health effects relative to long term exposure to multiples of persistent toxic chemicals.

The following are the recommendations as developed from the four theme groups (World Large Lakes Conference, 1986):

## 6.5.1 RECOMMENDATIONS OF THE CONFERENCE

### 6.5.1.1 Chronic Effects of the Toxic Chemicals in Large Lakes:

1. A new thorough international effort is required now to eliminate the major retrievable sources of persistent toxic chemicals from not only large lake ecosystems, but the global ecosystem. A preventative approach must be taken rather than the present reactive approach wich currently requires absolute proof of a cause/effect relationship, particularly proof of excessive risk to chronic human disease.

2. Human exposure and chronic health effects must be documented relative to long-term exposure to multiple persistent toxic chemicals in order to continue with regulations and decisions that require these data.

3. An inventory of sources for persistent toxic chemicals which are now prevalent within the ecosystem must be accurately obtained on a local, regional, national and global basis.

4. Hazard assessment protocols must be developed and used cooperatively on an international basis to allow for worksharing and to provide internationally consistent legal decisions on toxic chemical control.

5. International control agreements are still required to:
    a) eliminate hard pesticides such as aldrin/dieldrin, lindane and toxaphene; and
    b) provide for consistent and complete destruction of the major retrievable sources of persistent industrial chemicals.

6. Decisions on toxic chemical control must be based on a thorough, honest and complete public disclosure of information.

### 6.5.1.2 Consideration of Toxic Substances in Fisheries Management:

1. More research is needed to determine the value, both economic and social, of our large lakes.

2. A responsible organization is needed to coordinate information for the public on toxics in fish.

3. More research is needed to establish realistic, long-term tolerance levels for fish health, aquatic ecosystem health, using micro- and mesocosms, and for the health aspects related to human consumption of fish.

4. Standardization of monitoring contaminants in fish is needed for comparing long-term trends and an early warning system.

5. Continuing efforts are needed to reduce or stop inputs of contaminants to large lakes from both point and nonpoint sources.

6. Develop a procedure to bring the public, possibly through advisory groups, into working groups with scientists and resource managers to address contaminant problems.

### 6.5.1.3 Prevention of Toxic Contamination of Large Lakes Toward a World Management System for Sustainable Development:

1. Historically, large lakes represent a vital economic resource which has thus far not been fully appreciated.

2. There is a striking similarity between the socio-economic and political characteristics of the world's large lakes systems. This similarity is reflected in the multijurisdictional or international institutional arrangements developed to manage those systems.

3. The management of this resource is frequently rendered difficult by a multitude of political boundaries, often including international boundaries. Managing such transboundary environ-mental resources represents a major challenge to existing political institutions; therefore, a priority setting methodology to guide research and management efforts is essential. In the Great Lakes Basin, the Science Advisory Board and the Council of Research Managers are designed to serve this function. Concerted action should be directed at developing the membership of the Science Advisory Board and the Council of Research Managers so that their recommendations are incorporated into the research priority-setting mechanisms of the governments.

4. It is recommended that research be undertaken into institutional alternatives for integrating scientific inquiry and public policy into a single system for water management in large lake systems.

5. Further examination and research from socio-economic and legal-political perspectives must be undertaken to devise laws, policies and programs to protect the health and safety of citizens and which recognizes the primacy of the ecosystem boundaries while accommodating the realities of political jurisdiction.

6. Pollution is particularly threatening to large lakes, which tend to become a "sink" for pollutants from all sources. Traditionally pollution sources have been

characterized by environmental medium but it is becoming increasingly clear that the pathways of pollutants can lead through several media and that controls consequently must take a cross-media approach.

7. Research is needed to devise ways to prevent the formation of new hazardous wastes and to eliminate the hazards associated with those which already exist. Some corporations have substantially reduced the use of persistant toxics in manufacturing by substitution, reduction and complete recovery of those substances, at the same time protecting the environment and improving corporate profits. Other corporations should be challenged to do the same.

8. Intensive agricultural practices not only result in nonpoint pollution of air, land and water but also result in overproduction of foodstocks. Policy and technical research is needed to develop and apply socially and economically feasible alternative agricultural practices.

9. The huge mass and diversity of environmental data overwhelm our ability to comprehend their meaning. computerbased data and information management systems are needed to structure and organize this mass of information so that it becomes immediately useful to decision makers.

10. A fostering of communication among international commissions addressing shared aquatic resoureces would provide exchange of information on their successes and failures. Therefore, it is recommended that a conference of internatinal commissions be convened to address institutional arrangements and the role of international commissions in addressing prevention and remediation of transboundary pollution.

11. Large lakes can only be successfully protected if citizens are aware of the importance of the issue and have the means of expressing their awareness. Governments are encouraged to provide access to reliable information and to provide appropriate opportunities in their decision-making processes for participation by the public.

12. Developing countries appear to be readily accepting the technology of industrialized countries often without full recognition of the pollution consequences. There is an urgent need for communication between industrialized and developing countries on pollution prevention so that the pollution experiences of the more industrialized nations are not readily repeated.

13. Continuous and integrative scientific research on large lakes should be a high priority for governments.

14. The policy of the great Lakes Water Quality Agreement is reaffirmed, specifically the following section: "The philo-sophy adopted for control of imputs of persistent toxic substances shall be zero discharge." It is further recommended that governments implement programs advocated by the Royal Society of Canada and the National Research Council of the United States in their review of the Great Lakes Water Quality Agreement.

15. Recognizing that the Pollution from Land Use Activities Reference Group (PLUARG) study and report conducted under the auspices of the Internatinal Joint Commission was a landmark in the understanding of the role of nonpoint or diffuse pollution in North America and that it has served as a strong base for the development of new strategies to cope with this problem, it is proposed that a similar study be undertaken for toxics. Therefore, it is recommended that the governments of Canada and the United States request the International Joint Commission to undertake a major sutdy on an integrated approach to the management of toxic contaminants. The participation of the Great Lakes Fishery Commission in this study is encouraged.

### 6.5.1.4 Sources, Fate and Controls of Toxic Contaminants:

**Sources:**

1. There is a need to more effectively manage and regulate toxic substances on a global perspective. This approach must include developing nations. International efforts must utilize scientifically valid techniques for the collection of compatible data. The data thus developed should be shared by nations so that a global response to the toxic exposure problem may be developed.

2. Quantitative and qualitative source information needs to be enhanced to provide adequate information for establishing mass balances as a means of establishing causes and consequences. Sources include industries, municpalities, combined sewer overflows, agricultural and urban runoff, pollutants that are in-place in sediment, contaminated groundwater, etc.

3. Mediation of environmental impact (e.g., toxicity and bioavailablity) of in-place pollutants is needed.

4. It is recommended that developing nations be encouraged to use alternative approaches to persistent organochlorine compounds (e.g., DDT, toxaphene) to obviate the buildup of these compounds in large lake systems.

Energing techniques in agriculture and pest control should be made available to developing nations as soon as possible.

Controls:

1. Waste Reduction On-Site or Near Source: it is recommended that control be emphasized at or near the source through reuse, recycle, recovery and waste exchange.

2. Waste Treatment, Destruction and Disposal On-Site or Near Source: It is recommended that:

a) hazardous waste management begin immediately.

b) an integrated approach to toxic substance control consisting of combinations of biological, physical, chemical and high-temperature thermal unit processes be implemented, recognizing opportunities for adding to existing in-place technology.

c) centralized hazardous waste treatment facilities for the small to medium sized generators be utilized.

d) innovative sludge management approaches and techniques be implemented.

e) existing or newly developed, low-cost, rapid screening techniques (e.g., bioassays) for assessing toxicity be used so that appropriate technical responses can be implemented before environmental damage occurs.

f) increased use of available process selection protocols for identification of the most cost-effective processes be implemented.

g) improved operation of existing hazardous waste treatment facilities which ensure that toxic compounds are not created (dioxins through incineration) be implemented. The importance of adequate operator training programs must be recognized and addressed.

h) effective technology transfer and continuing education be carried out in both developed and developing nations.

## 6.7 MAJOR FINDINGS

a) The major findings of chapters 1 to 5 are consistent with and supported by those of the International Joint Commission

Great Lakes Water Quality Board, the International Joint Commission Human Health Effects Committee, the joint review of Great Lakes Water Quality by the U.S. National Academy of Science and the Royal Society of Canada, and of the World Conference on Large Lakes.

b) The chemicals of concern in all cases are consistent and emphasize persistent organic compounds such as PCBs, chlorobenzenes, chlorophenols, chlorinated dioxins and dibenzofurans and some persistent pesticides.

c) The sources to be remediated are consistent and chemicals derived from special waste are emphasized in municipal and industrial discharges as well as incineration, emissions, landfills, and contaminated sediments.

d) All of these documents emphasize the need for better treatment of special waste, a preventative approach, and better public information.

# APPENDIX A

## GREAT LAKES AREAS OF CONCERN FOR ONTARIO (FROM GREAT LAKES WATER QUALITY REPORT, 1985)

The following is a description of 15 Great Lakes areas of concern for Ontario as described by the International Joint Commission Great Lakes Water Quality Board (IJC, 1985). Usage of Great Lakes resources (eg. the fishery) is impaired due to contamination in these areas. By international agreement, these along with 27 U.S. areas of conern will be remediated so that the use of all Great Lakes resources affected by these areas can be restored.

### PENINSULA HARBOUR (Ontario)

#### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Conventional Pollutants | Industrial Point Sources |
| Heavy Metals | In-Place Pollutants |
| Toxic Organics | |
| Contaminated Sediments | |
| Fish Consumption Advisories | |
| Aesthetics | |

Foam and suspended solids have created adverse aesthetic problems near the outfall. Phenols in harbour waters, and heavy metals, including mercury and low levels of PCB from previous discharges occasionally found in sediments may adversely affect recreational fishing.

## JACKFISH BAY (Ontario)

### NATURE OF PROBLEM

#### Types of Problems

Conventional Pollutants
Heavy Metals
Toxic Organics
Contaminated Sediments
Fish Consumption Advisories
Biota Impacted

#### Sources of the Problems

Industrial Point Sources
In-Place Pollutants

Coliforms, phenolics, resins, aromatics, etc. found in Moberly Bay with coliforms carried into Jackfish Bay. Heavy metals and trace organics in sediments may be toxic to bottom dwelling organisms. Pollutants may adversely affect recreational fishing.

## NIPIGON BAY (Ontario)

### NATURE OF PROBLEM

#### Types of Problems

Conventional Pollutants
Heavy Metals
Toxic Organics
Contaminate Sediments
Fish Consumption Advisories
Biota Impacted
Aesthetics

#### Sources of the Problems

Industrial Point Sources
In-Place Pollutants

Coliforms, phenolics, resins, etc. from pulp and paper mill discharges extend south into the bay and may in part cause taste and odor problems in drinking water and adversely affect recreational fishing. Heavy metals in sediments.

## THUNDER BAY (Ontario)

### NATURE OF PROBLEM

#### Types of Problems

Conventional Pollutants
Heavy metals
Toxic Organics

#### Sources of the Problems

Industrial Point Sources
In-Place Pollutants

Contaminated Sediments
Fish Consumption Advisories
Biota Impacted
Beach Closings

Heavy metals, phenolics, resins, etc. in water and sediments are highest in the Kaministiquia River delta and adjacent nearshore area. Coliforms and heavy metals are found in waters throughout the bay with oxygen depletion in the delta area. Mercury in sediments from former waste discharges is believed to contribute to levels in larger fish. Recreational uses of water are adversely affected. Contaminated sediments require confined disposal of dredged materials.

## COLLINGWOOD (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Heavy metals | Municipal Point Sources |
| Toxic Organics | In-Place Pollutants |
| Contaminated Sediments | |
| Eutrophication | |
| Fish Consumption Advisories | |

Nutrient enrichment with sediments contaminated by heavy metals and PCB.

Mercury contamination of large perch, not attributable to local sources, requires fish consumption advisories.

Restricted disposal of dredged spoils required.

## PENETANG BAY TO STURGEON BAY (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Eutrophication | Unknown |

The natural phenomenon of limited exchange of Severn Sound with Georgian Bay believed to be largely responsible for delayed response to control programs.

## SPANISH RIVER (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Contaminated Sediments | Industrial Point Sources |
| Tainting of Fish Flesh | In-Place Pollutants |

Harbour sediments contain PCB, heavy metals, phenolic compounds, and wood chips; confined disposal of dredged spoil is required.

## WHEATLEY HARBOUR (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Conventional Pollutants | Municipal Point Sources |
| Heavy metals | Industrial Point Sources |
| Toxic Organics | In-Place Pollutants |
| Contaminated Sediments | Unknown |
| Eutrophication | |
| Fish Consumption Advisories | |

Oxygen depletion and high coliform levels are found in the surface waters of the harbour and periodically as far as the harbour mouth with coliforms extending into Lake Erie during spring runoff and peak canning season.

Limited sediment contamination with organic substances - PCB, DDT. Fish contaminated with mercury not attributable to local sources.

Confined disposal of dredged sediments required.

## BAY OF QUINTE (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Conventional Pollutants | Municipal Point Sources |
| Eutrophication | Industrial Point Sources |
| | Urban Nonpoint |

Despite reductions in phosphorus loadings, dissolved oxygen levels remain low in the Adolphus Reach and eutrophication still persists.

Zones of intermittently elevated bacterial levels occur as a result of stormwater discharges in the vicinity of Trenton, Belleville, and Picton.

## PORT HOPE (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Contaminated Sediments | In-Place Pollutants |
| | Waste Disposal Sites |

The sediment in the turning basin of Port Hope Harbour is contaminated with heavy metals, radium, uranium, and PCB. While the water column provides protection against exposure from the in-situ contaminants, dredging and disposal of this sediment has been identified as an environmental concern. Confined to the turning basin, the contamination results primarily from discharges made prior to 1945 as well as occasional contingency spills from Eldorado Nuclear.

## TORONTO WATERFRONT (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Conventional Pollutants | Municipal Point Sources |
| Heavy metals | Industrial Point Sources |

## HAMILTON HARBOUR (Ontario)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Conventional Pollutants | Municipal Point Sources |
| Heavy metals | Industrial Point Sources |
| Toxic Organics in Fish | Urban Nonpoint |
| Contaminated Sediments | Combined Sewer Overflows |
| Eutrophication | In-Place Pollutants |
| Fish Consumption Advisories | |
| Aesthetics | |

Municipal and industrial discharges, urban drainage, sediments, and algal decay increase oxygen demand. This oxygen demand depresses hypolimnetic dissolved oxygen levels, especially in the summer. This, in turn, limits the suitability of the deeper part of the harbour as a fish habitat.

Aesthetic quality is diminished by poor water clarity and colour, as a result of high levels of suspended solids, chlorophyll, and dissolved organics, thereby deterring broader recreational use of the harbour.

Significant levels of nutrients, several heavy metals, and PCB in the surface sediments from several portions of Hamilton Harbour. The problem is severe in Windermere Basin. Dredged material is disposed in confined areas.

Objectives are exceeded for total dissolved solids, zinc, ammonia, and phosphorus. Iron, cyanide, and phenolics also exceed the objective on occasion, especially adjacent to the steel mills on the south shore.

Levels of trace organics (PCB, PAH), phenols in fish under investigation.

## ST. MARYS RIVER (Ontario/Michigan)

### NATURE OF PROBLEM

| Types of Problems | Sources of the Problems |
|---|---|
| Conventional Pollutants | Municipal Point Sources |
| Heavy Metals | Industrial Point Sources |
| Toxic Organics | Urban Nonpoint |
| Contaminated Sediments | Combined Sewer Overflows |
| Fish Consumption Advisories | In-Place Pollutants |
| Biota Impacted | |

No problems exist along the Michigan shoreline.

Bacterial levels downstream from combined sewer overflows in Sault Ste. Marie, Ontario limit recreational use in some areas; mercury from residual upstream sources (possibly natural) is found in larger fish requiring advisories on consumption; sediments along shoreline carry high levels of ether solubles, heavy metals, and other contaminants and require confined disposal. Trace organics (PCB in sediments; PAH in sediments and biota) under investigation with objective of defining extent of problem and possible remedial measures.

## ST. CLAIR RIVER (Ontario/Michigan)

### NATURE OF PROBLEM

Types of Problems

Conventional Pollutants
Heavy Metals
Toxic Organics
Contaminated Sediments
Biota Impacted
Beach Closings
Fish Consumption Advisories

Sources of the Problems

Municipal Point Sources
Industrial Point Sources
Combined Sewer Overflows
In-Place Pollutants

Bacterial contamination from combined sewer overflows at Sarnia limits local recreational use.

Residual sediment contamination and, to a lesser degree, industrial discharges are slowing the recovery of the benthic fauna, adjacent to and downstream of the petroleum and petrochemical complex in Sarnia and Moore Township.

Trace organic contamination of water, sediment and fish identified but significance not known - studies proceeding.

Sediment at several locations along the Ontario shoreline of the St. Clair River remains contaminated with trace organics, PCB and heavy metals and requires confined disposal if dredged.

## DETROIT RIVER (Ontario/Michigan)

### NATURE OF PROBLEM

Types of Problems

Conventional Pollutants
Heavy Metals
Toxic Organics
Contaminated Sediments
Eutrophication
Fish Consumption Advisories
Biota Impacted
Beach Closings
Aesthetics

Sources of the Problems

Municipal Point Sources
Industrial Point Sources
Urban Nonpoint
Rural Nonpoint
Combined Sewer Overflows
In-Place Pollutants
Unknown

PCB and mercury levels in sediment of the Detroit River occur along the United States shore in the vicinity of the Detroit sewage treatment plant, Great Lakes Steel, and the Rouge River mouth. Recent levels of cadmium, chromium, copper and zinc at mouth of Rouge River are higher than those reported in 1973 and are attributable to combined sewer overflows. The benthic population along the shoreline near the mouth of the Rouge River remains highly disrupted, and contains high densities of sludgeworms indicating heavily polluted sediments.

Bacterial levels are elevated on both sides of the river *from storm* and combined sewer overflows, and treated municipal discharges. Recreational activities have been restricted. Phenolics and iron objectives are exceeded occasionally on the U.S. side, and improvement over the past 10 years.

Nutrient enrichment of surface waters mainly attributable to United States sources, continues to restrict recreational uses.

Elevated heavy metals and trace organics attributable to United States sources, continue to affect recreational fishing. Mercury levels remain elevated in certain species of sport fish, and consumption advisories remain in effect.

# APPENDIX B

## EXPOSURE AND TOXICITY PROFILES OF CHEMICALS FOUND IN THE GREAT LAKES

### B.1 1981 ANNUAL REPORT - COMMITTEE ON THE ASSESSMENT OF HUMAN HEALTH EFFECTS ON GREAT LAKES WATER QUALITY

In 1981 the Committee reviewed the toxicological data on 98 of the 296 chemicals identified in the Great Lakes by 1978. The following is a summary of the individual hazard assessments and recommendations reached at that time. The hazard assessments considered both potential toxicity and potential exposure. The mere identification of a Great Lakes chemical does not necessarily mean that it is present in concentrations which pose a hazard. Therefore it is as important to realize those chemicals on this list which were assessed not to be of concern as those which were considered a problem.

The following assessments are taken directly from the report.

#### ACETONE

Acetone is a synthetic solvent but also an intermediate product of bacterial decomposition of organic matter. Although widely used, this water miscible compound is highly volatile, readily diodegradable under both aerobic and anaerobic conditions and nonaccumulating. Measurable exposure to this compound is unlikely except locally during major accidental releases. Appendix E (I.J.C., 1978a) reports on detection of the compound in the water column in concentrations of 1 to 6 mg/L (one study).

Acetone is not acutely toxic orally and is unlikely to be of concern to human health on a long-term exposure basis unless vapour concentrations are high, locally. Monitoring is not recommended.

### ALDRIN

This synthetic insecticide is highly lipophilic and presumably accumulates in living tissue. There is no evidence of mineralization although it may be modified by microbial attack or slowly converted to dieldrin.

Appendix E (I.J.C., 1978a) shows occurrence in nearshore fish in Lakes Superior and Huron. It is found only rarely and no quantification is given.

Aldrin has potential for acute and chronic health impacts and is presently controlled. No additional monitoring is recommended over the existing program.

### ANILINE

This synthetic chemical is quite soluble, nonbioaccumulating and quite readily mineralized, e.g. in biological wastewater treatment plants. Although very large amounts are used by the chemical industry, significant local exposure is expected only in case of a serious accidental release. Appendix E (I.J.C., 1978a) cites occurrence in a waste effluent. No quantification is given.

Aniline is very acutely toxic, however, it is not thought to be a carcinogen and is unlikely to pose a threat to health unless inhaled. Monitoring is recommended for this compound in the event of industrial discharges.

## ANTHRACENE

Anthracene occurs in coal tar and is produced for the manufacture of dyes. It is insoluble in water and has a tendency to concentrate in lipids and on particulate matter. It is also mineralized slowly in aerobic aquatic environments and in soils. It is also volatile and photodegradable. Appendix E (I.J.C., 1978a) cites its occurrence (without quantification) in pike from the Detroit River. The compound may occur in fish from other rivers and pools with significant industrial pollution.

Anthracene in the Great Lakes is of minimal concern from a human health perspective. Quantifications in additional fish would be of interest if this can be accomplished with the monitoring of other, more toxic polynuclear hydrocarbons.

## ARSENIC

Arsenic is an element regularly monitored in water supplies. The element is of widespread occurrence in low concentrations. Its industrial uses are quite diversified. In addition, atmospheric emissions from coal burning are significant. Maximum observed concentrations in lake and tributary waters in the Great Lakes Basin are below 10 ug As/L, maximum concentrations in fish are below 0.5 ppm with the exception of bloater chubs from the open waters of Lake Huron (up to 2.26 +/- 0.13 ppm).

Arsenic compounds have varying acute toxicities but some could be of concern in the event of high local contamination. In addition it has chronic toxicity effects of concern to human health. The element appears to be adequately monitored for the purpose of public health protection.

## BENZENE

This petrochemical-derived and synthetic compound is extremely common as a solvent, as an industrial raw product and in motor fuels. From available data, annual usage in the Great Lakes Basin may be in the order of 1 million tons, with well over 1,000 tons released as waste and a greater amount emitted as vehicle exhaust. The compound is biodegradable, particularly under aerobic conditions. While higher concentrations undoubtedly will not persist in the environment, low-level background concentrations in the order of 1 to 5 ug/L can be expected to exist in many areas and are confirmed by the few studies that have been conducted. They most likely indicate a steady state condition of continuous inputs and biodegradation.

Benzene has a low acute toxicity and at existing levels in the Great Lakes is unlikely to pose a significant chronic health threat.

## BENZYL ALCOHOL

This compound occurs naturally in plants and is of interest here as a synthetic solvent and industrial solvent. Annual usage is probably in the range of 10 to 100 tons; the compound has been detected in an effluent but has not been quantified. Benzyl alcohol is quite soluble in water and not persistent in the aquatic environment. The compound does not bioaccumulate.

Benzyl alcohol is unlikely to be a cause for concern for human health due to its presence in the Great Lakes.

## BIS-(2-CHLOROETHYL)ETHER

This compound was detected in one effluent but was not quantified. It is discharged in Michigan in amounts not exceeding 5 kg/a. No other information is available. The compound is insoluble in water and volatile.

Limited toxicological data indicate that monitoring to determine ambient levels would be worthwhile.

## BORNEOL

This camphor-related chemical occurs naturally in plant material but it is also used in the synthesis of pharmaceuticals and antiseptics. It has been discovered as a minor constituent in pulp and paper mill effluent. It is readily biodegradable and not expected to lead to measurable human exposure from water in the Great Lakes.

Based on its biodegradability and low levels in water, Borneol is not of particular concern for human health due to its presence in the Great Lakes. Monitoring is not recommended.

## 1-BROMO-1-CHLOROETHANE

This compound is volatile and probably non-biodegradable. It is a raw product for the synthesis of fluorocarbons. It has been detected in wastewater discharges to the Great Lakes and in the water column of Lake Michigan in trace concentrations (1 to 2 ug/L). Significant exposure is unlikely, except in case of accidental release.

Although exposure is likely to be low, few data on its long-term effects on man or animals were found, hence no adequate assessment of hazard or risk can be made. Monitoring is not recommended except possibly in industrial effluents.

## 1,3-BUTADIENE

This important raw product for the manufacture of synthetic rubber is probably used in the Great Lakes Basin in significant quantities. It has been detected (but not quantified) in a discharge to the Detroit River. As a water-insoluble gas, however, it is not of concern as an aquatic pollutant.

Butadiene has an apparently low order of toxicity and water solubility. Dangerous exposures in the Great Lakes Basin are unlikely. Monitoring is not recommended.

## CADMIUM

Cadmium is widely distributed in the industrial environment. Discharges from smelters, oil and coal-fired power plants, the planting industry, pigment, textile and chemical plants contribute to the Great Lakes while diffuse sources (wear of paint coatings, metal corrosion) contribute cadmium to urban runoff and their associated sludges. The concentrations in Great Lakes waters are below U.S. drinking water standards, but maximum observed concentrations are within one order of magnitude of the standard and tributary concentrations may exceed the standard several fold. Concentrations in Great Lakes fish are below 1 ppm.

Cadmium has considerable acute and chronic toxicity and remains on the list of toxic metals that require monitoring for sources, fate and time trends.

## CAMPHOR

Camphor is a natural terpentine and is also produced synthetically. It has been discovered in trace amounts in Lake

Michigan; the source is unknown. Camphor is rapidly mineralized by an acclimated bacterial community and significant human exposure is not likely except when large amounts of the compound is handled.

Camphor is of little concern presently because of its low toxicity and the unlikelihood of exposure. Monitoring is not considered necessary.

## CARBOFURAN

This pesticide is produced and handled in large amounts in the basin. In agricultural use it is metabolized rapidly but the complete mineralization of its metabolites is a slower process. It does not bioaccumulate. Agricultural watersheds tributary to Lake Erie have shown concentrations of the compound of less than 1 ug/L.

Carbofuran is only of concern in the event of high local exposure. Routine monitoring is not required.

## CARBON DISULPHIDE

This compound has been detected in a discharge to the St. Clair River but no quantitative data are given. Carbon disulphide apparently still is used in chemical syntheses, but in most or all of its former end uses it has been replaced by other compounds. This compound is sparingly soluble in water and quite volatile. It is not biodegradable but of limited chemical stability.

Carbon disulphide is very acutely toxic and requires strict control of use and containment in industries and in transit. Monitoring in effluents may be useful however. Monitoring in the aquatic ecosystem is unproductive.

CARBON TETRACHLORIDE

Carbon tetrachloride is used in very large amounts in the chemical industry for synthese, but in most of its dissipative end uses it has been replaced by other compounds. Still, several hundred tonnes are discharged annually in waste streams and trace concentrations in the range of 0.09 to 0.047 ug/L have been detected. the compound is persistent and may accumulate slightly in living tissues.

Chronic effects, quantities in use and presence in the Great Lakes of carbon tetrachloride suggest that this compound should be monitored in Great Lakes waters and especially in waste water effluents.

CHLORDANE, CIS-, TRANS-

This pesticide has been discovered in fish from Lake Superior (0.06 to 0.59 ug/g) and Lake Erie (0.13 ug/L or less), in effluents to Lake Michigan (0.05 to 0.12 ug/L) and in the water column (0.00002 to 0.32 ug/L). The compound is persistent and shows accumulation in living tissue.

Monitoring programs already exist for chlordane in Great Lakes waters.

## CHLORINATED NAPHTHALENES

Appendix E (I.J.C., 1978a) gives no substantiation for their detection in the Great Lakes Ecosystem. These compounds are lipophilic and biodegradable to varying extents depending on the number and positions of the chlorine atoms. Existing information is clearly insufficient to assess exposure potential.

Chlorinated naphthalenes have potentially hazardous chronic effects. Monitoring data to adequately assess exposure is necessary to determine the risks this compound may pose for human health.

## CHLORINATED TERPHENYLS

Chlorinated Terphenyls have been identified in a discharge to the St. Clair River but not quantified or characterized in greater detail. No usage data are available. Biodegradability will vary with the number and positions of chlorine atoms. Available information is insufficient to assess exposure potential.

Chlorinated terphenyls have known chronic effects and need to be monitored in the Great Lakes in order to assess exposure to man.

## 2-CHLOROANILINE

This compound was detected in Muskegon wastewater effluent but not quantified. The compound is only slightly soluble in water but is not expected to be accumulated into living tissues. All isomers of chloroaniline are mineralized at moderate rates, e.g. in a secondary wastewater treatment.

Little toxicological data on chloroaniline were found hence no assessment of hazard can be made. Monitoring of effluents that have not been subjected to secondary wastewater treatment should be considered if chloroaniline is found to be toxic.

## CHLOROFORM

This compound is used in quantities of several million kg per year and discharged in quantities of several thousand kg per year. Trace concentrations of 1 to 10 ug/L have been found in the lakes and the Niagara River; chloroform is undoubtedly widespread. The compound is not degraded biologically but volatilizes easily from aqueous solution.

Monitoring for chloroform presently exists. Ambient concentrations are much lower than those produced in the chlorination of drinking water. Additional monitoring is recommended for industrial discharges only.

## 3-CHLORO-1-PROPENE

This compound is used in chemical syntheses and was detected in a discharge to the St. Clair River. It was not quantified. It is a volatile, lipophilic compound which may be biodegradable. No other data are available.

Chloropropene can adversely affect major organs, however quantitative exposure data for the Great Lakes are unavailable. This compound should be monitored in discharges, but is not likely to be of consequence or concern in the waters of the Great Lakes.

## CHROMIUM

Coal is an important source of chromium, but of significance here is its occurrence in hexavalent form in industrial discharges. In the Great Lakes, it can be expected to occur mostly in insoluble or inert forms containing the trivalent form. The hexavalent form can occur under natural conditions in water. Maximum concentrations of total chromium in Great Lakes water are below 50 ug/L, but much higher concentrations occur in industrial wastewater effluents. Great Lakes fish contain less that 0.7 ppm total chromium with an isolated finding of 1.8 ppm (bloater chub off Goderich, Ontario).

General monitoring for chromium exists but monitoring should concentrate on industrial effluents.

## COBALT

The sources and chemical forms of cobalt in Great Lakes waters are not well known. Natural sources may be important and organic complexes may be the predominant form in the environment. Cobalt occurs together with nickel and sources of the latter may contribute to cobalt as well. Industrial uses in alloys, catalysts, pigments do not supply the element in a form which is readily solubilized. Cobalt is an essential micronutrient and as with other heavy metals it forms an insoluble sulfide in anaerobic sediments. Water column concentrations in the Great Lakes are below 10 ug/L, isolated measurements of fish tissues show concentrations of 1 ppm or less.

Toxicity and quantity and use data indicate little need for monitoring in the Great Lakes.

## DDT AND METABOLITES

Appendix E (I.J.C., 1978a) cites water column concentrations of 0.00013 to 0.68 ug/L and concentrations in fish of 0.01 to 3.3 ug/g. Studies conducted in Ontario and New York indicate a continuing decline of concentrations in Great Lakes fish and fish eating birds since the use of DDT was discontinued.

Monitoring for DDT and its metabolites exists. Periodic studies of concentrations in fish in areas where concentrations are still high are still useful.

## DIAZINON

This biodegradable pesticide has been detected in agricultural watersheds tributary to Lake Erie in concentrations of less than 1 ug/L. It does not accumulate in living tissues.

Diazinon is acutely toxic but is at low concentrations in the Great Lakes and degrades rapidly. Monitoring is underway.

## DIAZOBENZENE

This compound is used in chemical syntheses and has been detected, but not quantified, in one industrial effluent. The compound is sufficiently biodegradable to be largely removed by biological wastewater treatment.

Because of the chronic toxicity of this compound some monitoring in industrial effluents should be considered.

## 1,2-DIBROMOETHANE

This compound with 1,2-Dichloroethane, is used as a lead scavenger in leaded gasoline. Concentrations of 6 ug/L were found in Lake Michigan. It is probably biodegradable in the environment but no information is available to predict rates of decomposition at very low concentrations. It is probably widely distributed in trace amounts because of spills and evaporation of gasoline; it is destroyed during combustion.

Dibromoethane (and dichloroethane) can have considerable acute and chronic effects on man; hence monitoring should be considered to determine ambient levels in air and water.

## DICHLOROBENZENES

Several thousand tons of dichlorobenzenes are present in Niagara Falls chemical landfills. They have been detected in concentrations of 1 to 18 ug/L in the waters of Lake Michigan and in unquantified amounts in the Saginaw River. Dichlorobenzenes are biodegradable in principle and mineralized at moderate rates by acclimated microbial communities, but removal from water in trace quantities is less certain. They are moderately lipophilic but only sparingly water soluble. Presently available data are not sufficient to assess the abundance and exposure risk for these compounds.

Dichlorobenzenes are toxic after long-term exposure and some have an acute toxicity, however, exposure in the Great Lakes is not well established. Monitoring should be considered.

### DICHLOROBENZIDINE 2,2- OR 3,3- (DCB)

This compound has been detected in influent waste streams of the Muskegon, Michigan treatment system, but not in the effluent, supporting the notion that the compound is biodegradable at moderate rates as are related compounds, e.g. aniline and the dichlorobenzenes. The compound is used in the manufacture of azo dyes and more information on usage and disposal in the Great Lakes basin is required to determine exposure potential.

Because of the chronic toxicity of DCB, monitoring of effluents is recommended to develop data on exposure.

### DICHLOROBUTADIENES

Dichlorobutadienes have been detected in a discharge to the St. Clair River. No identification or quantitation has been attempted. No other data on occurrence or use are available. The compounds are slightly lipophilic and possibly biodegradable. More information is needed to determine exposure potential.

Dichlorobutadienes have significant acute and chronic toxicity. More information on usage and disposal is needed to determine specific monitoring needs, however monitoring is necessary to determine exposure potential.

## DICHLOROETHANE

This compound is added to leaded motor fuels as a lead scavenger. Ontario discharges 300 000 kg/a to the Great Lakes. Emissions to the air are of similar magnitude. The compound is moderately volatile, slightly water soluble and slightly lipophilic. It is mineralized slowly by bacteria. The compound has been detected in lake water only once, but was not quantified. It may occur in trace quantities in the more populated basins but should be detectable by analytical methods used to identify other chlorinated solvents. See dibromethane (ethylene dibromide) also.

Dichloroethane has significant chronic toxicity and like dibromoethane is in widespread use. Monitoring should be considered.

## 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D)

This compound has been detected in concentrations of 0 to 3.9 ug/L in a detailed survey of agricultural watersheds draining into Lake Erie and it occurs in Lake Erie sediments (<8 ug/L dwt). E.S. watershed concentrations are apparently decreasing. In Ontario there is currently a ban on use. 2,4-D is slowly mineralized by an acclimated microbial community.

2,4-D is regulated and at present appears to be adequately monitored.

## DIELDRIN

Dieldrin is an organochlorine pesticide and readily bioaccumulated in living tissues. It occurs in Great Lakes fish in concentrations of up to 0.76 and occasionally in the water column in concentrations of up to 0.12 ug/L. For biodegradability, see Aldrin.

Monitoring programs for dieldrin already exist and appear to be adequate.

## DI(2-ETHYLHEXYL)PHTHALATE (DEHP)

Phthalate esters are ubiquitous in the human environment in low concentrations. Their wide distribution is consistent with the notion that they are released from many sources as a result of their incorporation into many industrial products. DEHP is detectable in most Great Lakes waters in concentrations from 1 to 6 ug/L, lower concentrations were found only in Lake Superior, the highest occurred in the Detroit River. Up to 5000 mg/kg dwt were found in Detroit municipal waste water sludges. DEHP is accumulated into fish; concentrations up to 1.3 ppm were found. As DEHP and the other phthalates are slowly but completely biodegradable in natural waters, the observed levels in Great Lakes waters probably reflect a steady-state condition of amounts entering the lakes and those disappearing by microbial action.

DEHP has significant chronic toxicity and is ubiquitously distributed in the environment. Although levels presently in the environment are unlikely to pose a hazard to health, monitoring programs should be initiated to determine trends in DEHP levels.

## DIISOBUTYLPHTHALATE (DIBP)

This product is widely used in industry, apparently mostly as a plasticizer. Recorded discharges are insignificant. The compound is quite lipophilic and therefore may accumulate in biological tissues. It is slowly mineralized by acclimated microbial communities but its degradation at very low concentrations is uncertain. The compound has been detected at 1 ug/L in Lake Michigan and may be widely distributed in trace concentrations.

Although no information on carcinogenicity exists, DIBP has significant chronic toxicity and monitoring for this phthalate is recommended.

## N,N-DIMETHYLANILINE

This compound occurs in still bottoms. Discharge data are not available. It was discovered in the influent, but not in the effluent, of the Muskegon, Michigan Wastewater Treatment System, confirming that the compound is biodegradable at a moderate or slow rate. Without additional data on usage and disposal, exposure cannot be assessed.

It is unlikely that this compound poses a health risk to man in the Great Lakes Basin, however, effluent monitoring for this compound could be considered.

## DIOXANE

This synthetic solvent has been detected only once and in trace concentrations (1 ug/L) in Lake Michigan. Dioxane is miscible with water and not biodegradable. No further information is available to assess its abundance in the Great Lakes.

Dioxane has significant chronic toxicity. More information on usage and disposal is needed to assess exposure potential prior to any risk assessment. Monitoring is recommended.

## ENDOSULPHAN (a-, b-)

This agricultural pesticide is found in the water column (0.002 to 0.25 ug/L, b form predominant) in sediment (up to 16.0 ug/g dwt, a and b forms) in air (up to 1.0 ppt) and rainwater (2.0 ppt, b form predominant). Use is by licensed application (which includes farmers) and is essentially without restrictions. Typical applications are in potato and tomato production. The compound is transformed by microbes to endosulphan-diol, but probably is not completely mineralized. Endosulphan is practically insoluble in water; data on bioaccumulation were not available from ISHOW.

Endosulphan has significant acute and chronic toxicity for man, however environmental levels are relatively low.

## ENDRIN

Endrin has been looked for extensively in the Great Lakes and its distribution is relatively well-known. Up to 0.52 ug have been detected in river and Georgian Bay fish, but levels are decreasing. Endrin accumulates in living tissues. It is metabolized by microorganisms to chlorinated ketones and aldehydes but is not mineralized. This pesticide is regulated and permits are given on a case-by-case basis (U.S.). New York DEC reports that no permits have been issued in recent years in the New York portion of the Great Lakes Basin.

Regulation and monitoring of endrin should continue.

## ETHION

This compound is related to malathion. 0.00002 to 0.00004 ug/L were found in the water column in one study, no other data are available. The compound appears to be sufficiently biodegradable to appear rarely, if ever, in water samples. It is not accumulated biologically. Use as a pesticide is restricted.

Ethion is extremely toxic on an acute basis but degrades rapidly. It is of minimal concern to health on a long-term basis and monitoring is not required.

## ETHYL BENZENE

The compound is very widely used in the Great Lakes Basin. Annual production or usage in New York is 120,000 lbs or 54,000 kg and in Ontario nearly 200 million kg. Ontario discharges 175 000 kg/a to the Great Lakes. Ethyl benzene is biodegradable to phenylacetic acid, by acclimated bacteria, but may persist in trace concentrations and in anaerobic sludges. One study has shown 1 to 2 ug of ethyl benzene in the water column.

High volume use of ethyl benzene coupled with chronic toxicity (inhalation) suggests air (and water) monitoring are advisable.

## FORMALDEHYDE

This compound has many uses and its annual use in the basin is in millions of kilograms. It has been detected in a discharge to the St. Clair River. Formaldehyde is a water-soluble gas and readily and rapidly mineralized in aqueous solutions of around 0.1% or lower. It will not normally be detected in the water column and as a result of its solubility and rapid degradation will not be accumulated into living tissues.

Monitoring in water is not required because formaldehyde degrades rapidly. Formaldehyde should be properly contained and spills and other major discharges prevented.

## GUAIACOL (METHOXYPHENOL)

This compound is a major component in effluents of the pulp and paper industry and has been identified in such discharges to Lake Superior. It is, however, readily and rapidly mineralized by microorganisms. It is quite soluble in water and is not accumulated into living tissues.

Although little information on toxicity was found the rapid degradation of guaiacol suggests monitoring is not necessary.

## HEPTACHLOR

Hepthachlor is less frequently detected in the environment than its oxidation product, heptachlor epoxide. It occurs in Great Lakes water in concentrations below 0.005 ug/L (except for the Detroit River water where it reached 0.02 ug/L). Rainwater over Lake Erie agricultural watersheds contained 7 ug/L, municipal effluents entering Lake Erie contained up to 0.035 ug/L. The compound was detected in Lake Superior fish but not quantified. Heptachlor and its oxidation products accumulate in living tissues and are persistent.

Heptachlor is presently monitored.

## HEPTACHLOR EPOXIDE

Heptachlor epoxide is the predominant persistent oxidation product of the pesticide heptachlor and it is itself biologically active. Heptachlor use is now severely controlled. The fate of its residues over time is not clear. Concentrations of the epoxide in Great Lakes tributaries have been from not detectable to about 10 ug/L; the highest concentrations were found in agricultural watersheds. The compound is widely distributed in Great Lakes fish in concentrations of 0.1-8 (in one case 28) ug/kg. Herring gull eggs in the Lakes Erie and Michigan watersheds contained about 0.2 (from 0.1-0.6) ug/g fresh weight.

Monitoring for heptachlor epoxide already exists.

## HEXACHLOROBENZENE (HCB)

Hexachlorobenzene has been found in fish from the lower lakes and the Niagara River (up to 0.025 ug/g) and Lake Superior (up to 0.04 ug/g) and in air over Lake Superior (2.8 ppt). Levels in fish eating birds have been declining since 1975. Figures on use and discharge are unimpressive, but the persistent nature of this compound and its strong tendency to accumulate in biological tissues make this compound a candidate for closer surveillance.

Although levels of HCB appear to be declining, monitoring should be considered to confirm that levels are continuing to drop.

## HEXACHLOROBUTADIENE (HCBD)

This compound has been detected but not quantified in fish from Lake Huron and the Ashtabula River. The compound is stable and is accumulated into living tissues. Available information is too scanty to permit estimates of exposure.

Acute and chronic toxicity data suggest that monitoring to establish levels in water and fish would be worthwhile

## HEXACHLOROBUTENE

The compound was detected in a tributary to Lake Erie at a concentration of 21 ug/L. The use pattern is not clear. The compound is probably not biodegradable. Information to assess exposure is presently insufficient.

The data available on toxicity and exposure are insufficient for even the most preliminary assessment of hazard or risk.

## HEXACHLOROCYCLOHEXANE (ALL ISOMERS EXCEPT LINDANE) (HCH)

Lake Huron fish contain up to 50 ug/g of the gamma and beta isomers. The alpha isomer was not found. Herring gull eggs from Lake Superior contained 0.03 +/- 0.02 mg/kg of the beta isomer. HCH isomers resemble lindane with regard to biodegradability and bioaccumulation.

Monitoring for hexachlorocyclohexane isomers should be considered although these are generally detected with lindane.

## HEXACHLOROETHANE

This compound was detected in one water column sample but was not quantified. It is produced or used in quantity. It is probably not biodegradable. It is lipophilic and likely to accumulate in living tissue. There is clearly no sufficient information to estimate exposure.

The chronic toxicity of this compound coupled with the lack of exposure data suggest monitoring be carefully considered.

### KEPONE (CHLORDECANE)

Not found in Great Lakes

Kepone has not been found in the Great Lakes and is not registered for use in the area. Monitoring is not recommended at this time.

### LEAD (INORGANIC)

Lead was singled out by the PLUARG group (I.J.C., 1978b) as the trace metal of concern in the Great Lakes. Contributions to the Great Lakes, via atmospheric transport from automotive sources and coal burning and from industrial wastewaters have been large, and the occurrence of the element in alkylated form has caused concern. The lowering of lead levels in automotive fuel and other controls have resulted in a decrease in atmospheric lead concentrations, but a decline in lead levels in the Great Lakes ecosystem thus far has not been documented. Concentrations of lead in Great Lakes waters are presently acceptable, but concentrations in tributaries (Milwaukee Harbor, Wisconsin; Grand River, Michigan) have been or are excessive. Concentrations in fish are generally below 0.5 ppm, with isolated findings of up to 1.5 ppm.

Continued monitoring and special studies on transport and fate of lead are recommended.

### LEOPTOPHOS

This pesticide is no longer produced or used in the basin. Appendix E (I.J.C., 1978a) lists its occurrence in rainwater (1100 ug/L, one positive result). The compound is very slowly metabolized in soil. There is no information on mineralization. It is strongly lipophilic and likely to accumulate in living tissue.

Monitoring is not required for this compound because it is no longer used in the Great Lakes Basin.

### LIMONENE

Limonene was found in concentrations of 130 to 500 ug/L in discharges from the forest products industry on Lake Superior. It is a naturally occurring compound and probably not stable in the environment.

Only a few toxicological data were found for limonene, however these data indicate it is not very toxic acutely and may not be very toxic chronically. Limonene probably degrades rapidly and hence exposure is likely to be low. Effluent monitoring may be warranted.

### LINDANE (A-HEXACHLOROCYCLOHEXANE)

Lindane has been found in Great Lakes water in concentrations of 0.00016 ug/L and 0.04 ug/g in fish (Lake Superior). Similar concentrations occur in wildlife. Air over Lake Superior contains 5 ppt of Lindane. Production and use are significant. The product is slowly mineralized, if at all. It is transformed biologically to other chlorinated compounds and it is concentrated in living tissues.

Monitoring as required now should be continued and should include fish and wildlife.

## MALATHION

This synthetic insecticide is produced and used in quantity in the Great Lakes Basin. It is rapidly degraded biologically and does not significantly accumulate in biological tissues. Appendix E (I.J.C., 1978a) indicates the infrequent occurrence (i.e., in less than 1% of the samples) in Ontario agricultural watershed tributary to Lake Erie.

Malathion poses a minimal health risk; it has low chronic toxicity and degrades rapidly. Monitoring is not required.

## METHYLMERCURY

Mercury has been introduced into the Great Lakes ecosystem by the widespread use in earlier years of mercury-containing wood product preservatives and by the chlor-alkali industry. Control of these sources has led to a decrease in concentrations of mercury both as total mercury and its alkylated forms. Increased coal burning may result in new significant inputs both locally and over large areas (through long distance atmospheric transport). The concentrations of mercury in Great Lakes water are presently not excessive, concentrations in fish are either acceptable or near-acceptable.

Problems of sample preservation and analysis of the different forms of mercury at very low concentrations have previously hindered work designed to examine the sources, forms of transport and the fate of mercury in the environment. As mercury is subject to biomethylation and subsequent bioaccumulation, an understanding of the movement of this element is important for its control. Emphasis should be on research and special studies in this field in addition to continued monitoring of water and fish.

## METHOXYCHLOR

This pesticide was detected in tributaries from agricultural watersheds at concentrations of 0.02 ug/L or lower, it was found in rainwater in the Lake Erie watershed (13.1 ug/L) and in wastewater effluents (up to 0.165 ug/L). Concentrations in fish ranged from not detectable to 0.05 ug/g. The compound accumulates in living tissue. Biodegradation proceeds slowly but much faster than for DDT.

Monitoring should continue.

## METHYL METHACRYLATE

Methyl methacrylate is a monomer or raw material in plastics (acrylics) manufacture. It is used in large amounts but probably not wasted regularly in significant quantities. It has been detected, but not quantified, in Lake Michigan waters. It is volatile, quite water-soluble, does not bioaccumulate and is subject to microbial degradation. Significant exposure is unlikely except during accidental release.

Methyl methacrylate generally has a low order of toxicity; monitoring is not recommended except on industrial waste streams.

## MIREX

Water column concentrations are reported in Appendix E (I.J.C., 1978a) as 0.00004 to 0.00068 ug/L (one study), concentrations in fish as 0.04 to 0.22 ug/g (Lake Ontario) and concentrations in wildlife to a maximum of 0.4 ug/g. Large amounts are still present in the Lakes, although use has been discontinued in the basin. Lake levels probably reflect disposal of mirex during manufacture. The compound is highly bioaccumulative and environmentally stable except for its slow conversion to 8-monohydromirex (photomirex).

Continued monitoring in fish and wildlife is recommended to document the decline in levels in the environment. Existing stocks should be disposed of properly.

## MONOCHLOROPHENOL

The isomer of the indicated CAS number was found but not quantified in a discharge to the Lower Fox River. No usage and discharge data are available, but the compound is likely to be present in many discharges and landfills of industries engaged in the production of chlorinated aromatic compounds. The monochlorophenols are moderately lipophilic and are mineralized by bacteria at moderate rates, except when chlorine is in the *meta*-position.

No assessment can be made until more exposure data are available. Chronic toxicity data is barely adequate. Monitoring is recommended only if sufficient quantities are determined to be in use.

## NAPHTHALENE

Naphthalene is used in millions of kilograms annually in the Great Lakes Basin. Discharges from Ontario are given as 300 kg annually. The compound was detected in trace quantities in several stations on Lake Michigan and in concentrations of 0.01 to 0.5 ug/g in Lake Huron and Lake Superior fish. It occurred in unquantified amounts in a discharge to the St. Clair river and in fish from the Detroit and Hamilton Harbor. Naphthalene is accumulated into living tissue but is also completely biodegradable. The slow rates of its mineralization are the result of its very limited solubility in water. Therefore, uptake by fish can occur wherever the compound is discharged in quantity.

The small amount of toxicology data available indicate naphthalene is of minimal concern to health in the Great Lakes Basin. Intermittent monitoring may be warranted.

## NICKEL

Nickel enters the Great Lakes Basin ecosystem from industrial discharges and to a lesser extent from the atmosphere, probably as a result of coal burning. Concentrations in the water column are below 100 ug/L, with tributaries rich in metal processing waste (Grand River, Michigan) at times showing slightly higher values. Fish data are scarce: up to 0.4 ppm have been reported for Lake Superior fish.

Emphasis should be placed on the control of industrial sources and a monitoring program to determine atmospheric deposition of nickel initiated.

## OXYCHLORDANE

The compound was detected in Lake Superior and Lake Huron fish in concentrations from 0.01 to 0.1 ug/g and in birds at Lake Michigan at 0.01 ug/kg. For properties refer to the profile for Chlordane.

The compound is of concern because of its presumed persistence. No assessment is possible at this time because of the lack of exposure and toxicity data.

## PENTACHLOROPHENOL (PCP)

This compound is widely used in wood preservatives, although use in highly concentrated form appears to have been somewhat restricted. It is widely distributed in Great Lakes waters (0.005 to 1.7 ug/L are reported in Appendix E (I.J.C., 1978a). Additional production and monitoring data are given in the 1980 Report of the International Joint Commission's Aquatic Ecosystems Committee. The compound is quite persistent and subject to bioaccumulation. PCP is also frequently contaminated with higher chlorinated dioxins.

A small scale monitoring plan for pentachlorophenol should be considered to provide trend data on PCP levels in water and wildlife (including fish).

## PHOTOMIREX (8-MONOHYDROMIREX)

Photomirex is a photo-oxidation product of mirex and has been detected in herring gull eggs at a concentration of 0.14 +/- 0.12 ppm. It is thought to be persistent. Concentrations in fish are presently decreasing as are the concentrations of the parent compound, mirex.

Photomirex has considerable chronic toxicity and monitoring for levels in fish and wildlife is worthwhile.

## POLYAROMATIC HYDROCARBONS (PAH'S):
## BENZO(A)PYRENE
## CHRYSENE
## DIBENZ(A,H)ANTHRACENE

These three polycyclic hydrocarbons are treated together here because of their similarity in origin, distribution and properties. Benzo(a)pyrene is widely distributed in the environment in low concentrations. Like with the other two compounds, it is mostly derived from combustion processes and occurs in coal tar. Coke ovens have been a major source. Other major sources are incinerators and runoff from streets where both the asphalt surface and diesel emissions are contributors. The compound is mineralized slowly by acclimated microbial communities in soils and in aquatic (aerobic) environments. It occurs in particulate form in water. It has been found in algae and accumulates in fish tissue. The reason may be that it is accumulated faster that it is degraded. Appendix E (I.J.C., 1978) shows water column concentrations of 0.2 to 0.3 ug/L and concentrations in fish fillets from the Detroit River and Hamilton Harbor of 14 to 128 ug/kg.

Chrysene has been identified in fish from the Detroit River and Hamilton Harbor and is probably of widespread occurrence in similarly polluted environments. Although slowly degraded by bacteria, uptake and accumulation into living tissues may be a more efficient process.

Dibenz(a,h)anthracene was detected but not quantified in fish from the Detroit River and from Hamilton Harbor. No further information is available. Properties are similar to Benzo(a)pyrene and Chrysene.

Exposure data for these hydrocarbons, both singly and as a group are not sufficiently developed for a definitive assessment of exposure and risk. Removal of particulate matter at water works may effectively reduce human intake from drinking water; body burdens from inhalation and food stuffs are likely to be much higher than those from drinking water. Based on their carcinogenicity they should be considered for monitoring.

## POLYBROMINATED BIPHENYLS (PBBs)

The numerous PBBs are treated here as one group. While one incident of their inadvertent introduction into livestock has been investigated and widely publicized, their true distribution is not completely known. Water column concentrations have been reported as 0.4 to 9.8 ug/L, concentrations in fish at 2.8 ppm (tributary to Lake Huron), duck breast tissue was found contaminated with up to 2.7 ppm. Usage in New York State is given as 2.3 t/a. PBBs are banned in Canada. The PBBs of lower chlorine content are slowly diodegradable as are the polychlorinated biphenyls.

PBBs have sufficient chronic toxicity that monitoring of use and ambient concentrations is recommended.

## POLYCHLORINATED BIPHENYLS (PCBs)

These compounds persist in the Great Lakes Basin ecosystem and are found in fish in concentrations exceeding 5 ug/g, particularly in the upper Great Lakes. They are detectable also in air and water column samples. PCBs will continue to be added to the Great Lakes from past uses, as equipment containing them is decommissioned or PCB-containing components are discarded. PCBs are very stable compounds. They are mineralized by bacteria only if chlorine substitution is low.

Continued monitoring of PCBs in fish and wildlife is recommended.

## SAFROLE

Safrole may occur as a minor component in waste effluents in the forest products industry. It was tentatively identified in one such discharge to Lake Superior. No quantification was given. The compound is probably biodegradable.

Although neoplasms have been observed in animals fed high doses it is unlikely that safrole is a significant threat to human health in the Great Lakes Basin. Monitoring is not recommended.

## SALICYLIC ACID

This compound appears to be used in moderate amounts in the chemical industry. It is also an intermediate in the microbial decomposition of naphthalene and some of its derivatives. It is inhibitory to bacteria in high concentrations but rapidly mineralized in low concentrations. It is water soluble and does not accumulate in living tissues. It was detected in Muskegon, Michigan, wastewater but was absent from the final effluent.

Based on the toxicity data available and exposure in the Great Lakes it is likely that salicylic acid is of minimal concern.

## SELENIUM

The Great Lakes are located in a region which is not naturally rich in selenium. Selenium compounds enter the Great Lakes from industrial discharges, the decay of products containing selenium and from the atmosphere as the result of coal burning. Rainwater in the Lakes Ontario Basin was found to contain 1 ug/L selenium. Concentrations in the water columns do not exceed 3 ug/L (2 ug/L found in Lake Michigan epilimnion up to 4.8 ug/L in the hypolimnion). Tributary waters contain less than 5 ug/L. Bioaccumulation factors for selenium are in the range of 2000 to 6000. Fish in the Great Lakes contain 1.5 mg/kg or less on a fresh weight basis.

Selenium is presently being monitored.

## SILVER

Silver has been included in the list of trace metals to be monitored in drinking water in the U.S. In fact, however, reclaiming of silver from effluents of the major users has made contamination extremely rare. The highest values for this element in waters of the Great Lakes and their tributaries reported in Appendix E (I.J.C., 1978) are 9 ug/L, tissues of fish and wildlife apparently have not been analyzed but significant contamination is unlikely.

This element is being monitored, probably excessively so and is of no further concern for the purposes of this investigation.

## SILVEX (2,4,5-TRICHLOROPHENOXYPROPIONIC ACID)

Appendix E (I J.C., 1978a) shows that this compound was looked for in the waters of Lake Superior but not detected. No other information is given. Silvex is a synthetic herbicide which formerly was used extensively in landscaping and on rights-of-way, but its use has become more strictly controlled and has decreased accordingly. Silvex is lipophilic and has a potential for accumulation into living tissues, but it is also rapidly mineralized by bacteria.

Monitoring for silvex presently occurs.

## STYRENE

Styrene has been detected in the City of Cleveland water supply but was not quantified. it was also detected in a discharge to the St. Clair River. Styrene is handled in very large amounts by the chemical industry. Styrene is slightly soluble in water and lipophilic; bioaccumulation data are not available. Styrene is degraded by microorganisms with the formation of more water soluble aromatic alcohols and acids as intermediate products. Complete mineralization occurs in the presence of an acclimated microbial community.

Large amounts of styrene are consumed in the Great Lakes Basin. The limited toxicology data suggests that monitoring should be considered.

## 2,3,7,8-TETRACHLORODIBENZODIOXIN (TCDD).

This compound has entered and continues to enter the Great Lakes Basin ecosystem as a contaminant in pesticides and herbicides, as a product of the incomplete combustion of other chlorinated compounds and from waste chemical dumps. It is not detectable in the water column by present techniques but is found in Lake Ontario fish at concentrations of several parts per trillion and in fish-eating birds in this lake.

2,3,7,8-TCDD has considerable acute and chronic toxicity. Monitoring of fish for this and other chlorinated dioxins is recommended. Current levels in water are unlikely to be a health concern.

## TETRACHLOROETHANE (TCE)

Tetrachloroethane is a solvent and chemical used in chemical syntheses. It was found in water column samples in concentrations of 1 to 44 ug/L. No other data are available. The compound is volatile and poorly, if at all, mineralized by bacteria.

Tetrachloroethane is quite toxic on an acute exposure basis; however, it is unlikely to pose a chronic health hazard. Monitoring may be required to obtain a better understanding of the distribution of this compound. Tetrachloroethane should be detectable in drinking water supplies using established methods.

## TETRACHLOROETHYLENE

Tetrachloroethylene is one of the most common solvents used in dry cleaning and in many other operations. Production and use in New York are over 45 000 t/a, in Ontario nearly 13 000 t/a. Annual discharges from Ontario to the Great Lakes are estimated as 25 000 t, with additional amounts escaping to the atmosphere. The compound is volatile and poorly, if at all mineralized. It is probably ubiquitous in the Great Lakes in trace concentrations.

Tetrachloroethylene is in widespread use and has chronic toxicity of concern. Monitoring to determine distribution in the Great Lakes Basin is recommended. It is readily detectable in drinking water and effluents by established methods.

## TETRAHYDROFURAN

Water column analysis cited in Appendix E (I.J.C., 1978a) has shown concentrations of 1 to 318 ug/L. This compound is a common reagent and solvent and probably handled in large amounts. It is water miscible. Information on biodegradability could not be located. Information is presently insufficient to assess exposure potential.

There are inadequate toxicity and exposure data to determine requirements for monitoring or to assess hazard and risk to health.

## TOLUENE

Toluene was detected in trace concentrations (1 to 5 ug/L) in Great Lakes water and in concentrations of up to 58 ug/L in the Niagara River. Toluene is used in amounts of hundreds of millions of kilograms per year and is a component of motor fuels. Ontario estimates discharges to the Great Lakes of 203 000 kg/a. Additional amounts are evaporated into the atmosphere. Toluene is slightly soluble in water. It is mineralized by an acclimated microbial community, but at the low concentrations which are found in aqueous media, decomposition is slow. Its wide distribution in trace concentrations in water and air is not surprising and may represent a steady state between discharges and atmospheric inputs on the one hand and degradation on the other.

Toluene is unlikely to pose a health hazard (in water or air) based on available toxicology data. Some intermittent monitoring of industrial discharges may be worthwhile.

TOXAPHENE (CAMPHECHLOR)

The group of compound known as the pesticide Toxaphene has been found in Lake Superior and Lake Huron water in concentrations of 0.1 to 1.0 ug/L. It was also detected in fish off Sheboygan, Michigan, in concentrations up to 4 ug/g. Data on usage are scanty (New York: 519 lbs annually). Toxaphene is highly lipophilic and probably not biodegradable. Additional information on its occurrence may emerge from the drinking water surveillance programs currently in effect in the U.S.

Toxaphene has significant acute and chronic toxicity and is currently being monitored.

TRICHLOROETHYLENE

This is another very common chlorinated solvent which has many applications, e.g. in metal cleaning and by the nature of its many end uses is widely distributed in the environment. Usage is in the millions of kilograms; Ontario estimated discharges of 13 600 kg annually and Michigan estimates discharges of 1 000 to 9 800 kg/a. Great Lakes concentrations range up to 10 ug/L. Trichloroethylene is volatile and poorly if at all mineralized by microorganisms.

It is recommended that trichloroethylene be included in monitoring of drinking waters and effluents by established methods. The widespread use of trichloroethylene suggests the need for monitoring data to establish the risk for human health.

## TRICHLOROPHENOLS 2,4,5- AND 2,4,6- (TCP)

The trichlorophenols are handled in millions of kilograms and are present in similar amounts in some chemical landfills in the basins from where they may leach into local runoff. The solubility of 2,4,6-trichlorophenol is 280 mg/L. Up to 100 ug/L were found in effluents to the Lower Fox River. The 2,4,5-isomer was detected in Lake Michigan waters but not quantified (I.J.C., 1978a). The 2,4,5-isomer is biodegraded poorly if at all, whereas the 2,4,6-trichlorophenol is degraded at a moderate rate, but the nature of the end products has not been determined. Both compounds are strongly lipophilic and may accumulate in living tissues.

Available information is clearly insufficient to allow an assessment of exposure of humans to these compounds. Hence monitoring should be considered.

## 2,4,5-TRICHLOROPHENOLXYACETIC ACID (2,4,5-T)

The herbicide 2,4,5-T is produced and used in significant amounts in the basin. It has been discovered in sediments in Lake Erie (up to 14 ug/g dwt) and the Detroit River and Lake Huron (not quantified). It also has been detected in air. 2,4,5-T is degraded slowly by acclimated microbial populations but information on complete mineralization is lacking. Contamination (depending on the production process) with tetrachlorodibenzodioxins must be considered.

2,4,5-T ought to be monitored in the Great Lakes Basin as are 2,4-D and 2,4,5-TP (Silvex).

## TRICHLOROTRIFLUOROETHANE (FREON)

This volatile chlorofluorocarbon has been detected in the water column at concentrations of 2 to 30 ug/L in one study. The compound is only very sparingly soluble in water and stable. No other data are available.

Although acutely toxic, it is unlikely that long-term exposure to trichlorotrifluoroethane is a concern for human health. Some monitoring data would assist future assessments.

## TRIPHENYL PHOSPHATE (TPP)

This compound was found in fish in Muskegon Harbor in concentrations of 0.06 to 0.12 ppm. The compound is highly lipophilic and likely to accumulate into living tissues. There are no data on biodegradability.

The available information is clearly insufficient to assess the distribution of this compound or its toxicity.

## VANADIUM

Vanadium has been associated with the burning of heavy oil and may reach the Great Lakes via the atmosphere. Smaller amounts occur in iron ores and generally in rocks and soils. Industrial applications (alloys) will not readily provide soluble forms of vanadium. Vanadium is a micronutrient for photosynthetic organisms. Few monitoring data are available. Concentrations in Lake Michigan are 26 ug/L or lower; maximum concentrations found in fish from Lakes Huron, Superior, and Michigan are 0.08 to 0.26 ppm.

Monitoring for vanadium can assist in the characterization of atmospheric particulates to indicate their source and would assist the risk assessment process by providing data on exposure. High concentration short-term exposure is of concern.

## VINYL BROMIDE

This compound was found in a discharge to the St. Clair River but not quantified. No other data are available. Vinyl bromide is lipophilic but its potential for bioaccumulation is uncertain.

Data are insufficient to assess distribution and potential for human exposure. This compound should be detectable by established methods of drinking water and effluent monitoring. Monitoring is recommended until a risk assessment can be made. Vinyl bromide may have similar toxicological properties to vinyl chloride.

## VINYL CHLORIDE (VC)

Vinyl chloride was detected in 11 discharges to the St. Clair River but was not quantified. Vinyl chloride is a gas, but soluble in water at a level of 1 mg/L. It is moderately lipophilic and the potential for bioaccumulation may be slight. Its volatility may provide a mechanism for removal from aquatic systems. Concern is primarily with groundwater contaminated by leachate from chemical landfills containing chlorinated ethylenes.

Quantification of vinyl chloride in effluents and water is recommended. This compound is detectable with established methods for monitoring drinking water and effluents for volatile halogenated organics.

## XYLENES

The xylenes are used as industrial chemicals and as solvents. They are a component of leaded gasolines. Ontario alone handles over 100 million kg annually and discharges 37 000 kg/a to the Great Lakes. Additional amounts are dissipated into the atmosphere from the use of xylene as paint solvents and in gasoline. One study cited in Appendix E (I.J.C., 1978a) shows 19 ug/L of xylenes in Lake Michigan. The xylenes are less soluble in water than benzene or toluene and are biodegradable at moderate rates by acclimated microbial communities. The low concentrations found are likely to be the result of continuous inputs and slow biological degradations.

It is unlikely that xylenes pose a hazard to health in the Great Lakes Basin, however, intermittent effluent and air monitoring would be useful.

## B.2 1986 ANNUAL REPORT - COMMITTEE ON THE ASSESSMENT OF HUMAN HEALTH EFFECTS OF GREAT LAKES WATER QUALITY

This recent report states very clearly which chemicals pose a human health concern. It includes data from a 1983 Inventory of chemicals found in the Great Lakes Basin. The following assessments are taken directly from the committee report.

### Pesticides

### ALACHLOR

Alachlor is a pesticide used primarily in the Lake Erie and Lake Ontario basins. It has been found in tributaries of Lakes Ontario, Erie, St. Clair and Huron in concentrations which are mostly below 1 ug/L but occasionally, particularly in the Sandusky and Maumee River basins, has reached mean concentrations of 1, 10 and even 100 ug/L (I.J.C., 1983a). Alachlor has not been reported in fish.

The Committee concludes that the levels of alachlor reported in surface water of some river basins are at a level of concern for human health. Further surveillance and assessment in these areas are warranted. The Committee recommends an interim maximum daily exposure limit of 0.5 mg/adult.

### ENDOSULPHAN

This pesticide has been reported, over the years, in numerous analyses of ambient water and rain in large parts of the Great

Lakes basin. It appears, however, that concentrations are decreasing (I.J.C., 1978a; I.J.C., 1983a). Endosulphan has not been reported in fish.

Reported concentrations in water are below a level of concern for human health, nevertheless, monitoring for this compound should continue. The Committee recommends an interim maximum daily exposure limit of 280 ug/adult based on the slightly more conservative EPA value (relative to other regulatory agencies such as the USFDA).

## HEXACHLOROBENZENE (HCB)

This contaminant is found extensively in water and fish in the Great Lakes. The highest concentrations most recently observed in fish are 0.03 mg/kg in northern Lake Huron (I.J.C., 1983a), 0.11 mg/kg and 0.23 mg/kg in eastern Lake Ontario (Oswego and Cape Vincent, I.J.C., 1983a) and 0.03 mg/kg (southern Lake Michigan, I.J.C., 1983a). Concentrations in most open lake waters are at or below 1 ng/L; however, mean concentrations in parts of the Niagara River, Lake Ontario and tributaries to Lake Superior have reached 20, 27 and 15 ng/L, respectively (I.J.C., 1983a).

The concentrations of HCB reported in fish and water are at a level of concern for human health. The Committee recommends careful evaluation of the levels in these areas.

## OXYCHLORDANE

Oxychlordane concentrations have been determined in numerous fish samples. The highest concentrations were found in fish from the central and southern basins of Lake Michigan and the open waters of Lake Superior (0.1 mg/kg, (I.J.C., 1978a)). Other mean values from a series of measurements from fish in Lake Superior, northern Lake Michigan and western Lake Ontario are similar (0.02 to 0.1 mg/kg, I.J.C., 1983a).

Reported concentrations in fish are at a level of concern for human health. Further surveillance and assessment is warranted in these areas. The Committee recommends an interim maximum daily exposure limit of 0.44 ug oxychlordane/adult, based on the U.S. EPA risk assessment for chlordane.

## PENTACHLOROPHENOL (PCP)

The highest reported concentrations of pentachlorophenol in the two listings for the Great Lakes basin were 8.5 ug/L in the lower Niagara River in 1979, (I.J.C., 1983a) and 155 ug/kg in yellow perch and 260 ug/kg in brown bullhead caught in 1978 in the Bay of Quinte, Lake Ontario (Fox and Joshi, 1984).

The concentrations reported in the two inventories are just below a level of concern for human health. However, this compound is still widely used and continued surveillance is desirable. Furthermore, PCP levels may serve as a useful indicator of contamination with chlorinated dibenzo-p-dioxins and dibenzofurans. The Committee recommends an interim maximum daily exposure limit of 0.21 mg/adult based on the WHO and NAS ADI values.

## SIMAZINE

The concentrations of this pesticide in water have been extensively studied throughout the basin. Except for one isolated measurement of 10 ug/L, the values are below 2 ug/L and mostly between 0.2 and 0.02 ug/L. Simazine has not been reported in fish.

The concentrations of simazine reported in water in the 1983 Inventory are not at a level of concern for human health. The Committee recommends an interim maximum daily exposure limit of 15 mg/adult based on the ADI of the NAS.

## 2,4,5-TRICHLOROPHENOXYACETIC ACID

Maximum reported concentrations in water of this compound are 300 to 800 ng/L, with the mean values of the several series of measurements under 100 ng/L (several tributaries to Lakes Erie, Huron and Ontario, 1983 Inventory). Appendix E (I.J.C., 1978a) does not give concentrations of the compound in water or fish.

The reported concentrations of 2,4,5-T per se in water are not at a level of concern for human health. Past contamination of this compound with chlorinated dibenzo-p-dioxins and dibenzofurans should be noted and levels of 2,4,5-T may indicate environmental contamination with these chemicals. The Committee recommends an interim maximum daily exposure limit of 7.0 mg/adult based on the ADI of the NAS.

### TRIFLURALIN

This pesticide has been found in several tributaries to Lakes Erie and Michigan in concentrations of several tenths of 1 ug/L (IJC, 1983a). Trifluralin has not been reported in fish.

The published levels of trifluralin in water are not at a level of concern for human health. The Committee recommends an interim maximum daily exposure limit of 7 mg/adult based on the ADI of the NAS.

## Halogenated Hydrocarbons

### CARBON TETRACHLORIDE

Carbon tetrachloride has been detected at a concentration of 47 ng/L in Lake Erie (I.J.C., 1978a) and at concentrations up to 18 ng/L in the lower Niagara River and from 0 to 25 ng/L in Lake Ontario (Kaiser, et al., 1983). The I.J.C. 1983 Inventory (I.J.C., 1983a) lists concentrations up to 47 ng/L in two segments of Lake Erie off Sandusky, Long Point and Erie for the years 1977 and 1978. The Genesee River at Rochester showed a mean concentration of 2 ug/L (I.J.C., 1983a). Levels in fish are not reported and are unlikely to be found. The lower Genesee River is not a source of drinking water, but forms a plume along the southern shore of Lake Ontario, where water supply intakes are located.

Carbon tetrachloride is at a level of concern for human health in the Genesee River, based on reported data. The Committee recommends that sources in the Great Lakes require identification and evaluation.

## 1,2-DICHLOROETHANE

1,2-Dichloroethane has been detected at several locations in the Great Lakes basin. The highest concentrations (4 ug/L) were observed in Fields Brood, a tributary to Lake Erie at Ashtabula, Ohio (I.J.C., 1978a). A mean concentration of 3 ug/L was found in 1982 in the Genesee River, a tributary to Lake Ontario at Rochester (I.J.C., 1983a). 1,2-Dichloroethane has not been reported in fish.

The reported concentrations of 1,2-Dichloroethane in water are at a level of concern for human health. Therefore, the Committee recommends that monitoring continue and that this situation be carefully evaluated.

### 1,2-DIBROMOETHANE

EDB was reported at a concentration of 6 ug/L in Indiana Harbor, Lake Michigan (I.J.C., 1978a). The 1983 Inventory does not contain findings of this compound.

The occurrence of EDB in water reported for Indiana Harbor is at a level of concern for human health. Monitoring for EDB in other areas of the Great Lakes basin is recommended.

### HEXACHLOROETHANE (HCE)

HCE was reported in Fields Brook, a tributary to Lake Erie in Ohio, at 3 ug/L (I.J.C., 1978a). The 1983 Inventory (I.J.C., 1983a) lacks details on several findings in the summary for the Lake Ontario Basin. HCE has not been reported in fish. The concentration of HCE in Fields Brook is at a level of concern to human health as defined by the Committee. Current levels of HCE in the waters of Fields Brood and other areas of the Great Lakes are unavailable.

The Committee recommends an interim maximum daily exposure limit of 48 ug/adult based on the U.S. EPA risk estimates.

### 1,2-DICHLOROETHENE (DICHLOROETHYLENE, CIS- OR TRANS-)

1,2-Dichloroethene has been detected in discharges to the Great Lakes (e.g. the Detroit River) but not quantified (I.J.C., 1978a). The 1983 Inventory notes the compound's absence in Lake Ontario. It has not been reported in fish and is unlikely to be found.

There are no data to indicate whether or not 1,2-Dichloroethene is at a level of concern for human health. The Committee recommends monitoring to confirm its absence or presence.

### TRICHLOROETHENE (TRICHLOROETHYLENE)

Trace concentrations are widely found in the Great Lakes basin. Positive results are reported generally from the same locations that indicate the presence of tetrachloroethene. The maximum concentration reported is from Fields Brook, a tributary to Lake Erie at Ashtabula, Ohio (188 ug/L), (I.J.C., 1978a). Other reported concentrations are up to 11 ug/L in the Niagara River and up to 33 ng/L in Lake Ontario (Kaiser, _et_ _al._, 1983). Trichloroethene has not been reported in fish and is unlikely to be found.

Several reported concentrations of TCE in water are at a level of concern for human health. The Committee recommends further monitoring and evaluation of water.

### TETRACHLOROETHENE (TETRACHLOROETHYLENE)

High concentrations of this common solvent were reported in Fields Brook, a tributary to Lake Erie at Ashtabula, Ohio (45 ug/L), (I.J.C., 1978a). Highly variable concentrations were found in the Niagara River (0-134 ug/L, I.J.C., 1983a; Kaiser, _et_ _al_., 1983). In Lake Ontario readings were below 15 ng/L, except for one higher value (Kaiser, _et_ _al_., 1983). Concentrations between 1 and 10 ug/L were found in several other tributaries and discharges. Tetrachloroethene was not reported in fish and is unlikely to be found.

The highest concentrations of tetrachloroethene reported in surface water are at a level of concern for human health. The Committee recommends further monitoring and evaluation of water.

## VINYL CHLORIDE
## VINYL BROMIDE

Both compounds were detected in discharges into the Detroit River (I.J.C., 1978a; I.J.C., 1983a). No quantification was provided. Both compounds are volatile and poorly soluble like many other chlorinated solvents. They have not been reported in fish from the lakes and are unlikely to be found.

There are no data to indicate whether or not vinyl chloride and vinyl bromide are at a level of concern for human health. The Committee recommends that the presence of both compounds in discharges be confirmed and quantified.

## 3-CHLORO-1-PROPENE (ALLYLCHLORIDE)

3-chloro-1-propene was detected in discharges to the Detroit River but was not quantified (I.J.C., 1978a). A concentration of 3 ug/L was reported from Wine Creek, a small tributary to Lake Ontario which drains the PAS chemical waste disposal site near Oswego, New York (I.J.C., 1978a). The compound is not listed in the I.J.C., 1983 Inventory.

There are insufficient data to indicate whether or not 3-chloro-1-propene is at a level of concern for human health. The Committee recommends monitoring at or near industrial discharges to confirm the presence or absence of the compound.

## 2,3-DICHLOROBUTADIENE

This chemical occurred in discharges to the Detroit River but was not quantified (I.J.C., 1978a).

The Committee recommends that the presence or absence of 2,3-Dichlorobutadiene be determined in industrial discharges. If detected in water or fish, toxicology research may be required to develop an interim exposure limit.

## HEXACHLOROBUTADIENE (HCBD)

High levels of this compound (mean value of 2.18 mg/kg) were found in lake trout from Lake Superior (several locations, exclusive of the Isle Royale area), (I.J.C., 1983a). Concentrations of 22 ug/L were reported in water from Fields Brook, a tributary to Lake Erie located at Ashtabula, Ohio (I.J.C., 1978a).

Concentrations of HCBD reported in fish from Lake Superior and in water from Fields Brook are at a level of concern for human health. The Committee recommends monitoring and evaluation of human exposure to HCBD via water and fish in these areas.

## 1,2-DICHLOROBENZENE (O-DICHLOROBENZENE, ODB)
## 1,3-DICHLOROBENZENE (M-DICHLOROBENZENE, MDB)
## 1,4-DICHLOROBENZENE (P-DICHLOROBENZENE, PDB)

The dichlorobenzenes are common contaminants in fish and water samples taken from the Great Lakes and their tributaries. Maximum observed concentrations for the three contaminants in water are 0.007, 0.002 and 0.064 ug/L, respectively. Highest mean concentrations in fish were 0.001, 0.003 and 0.004 mg/kg, respectively (Western Lake Ontario, Western Lake Erie), (I.J.C., 1978a; I.J.C., 1983a).

Concentrations of dichlorobenzenes reported in fish and water are below a level of concern for human health. The Committee recommends an interim maximum daily exposure limit of 0.94 ug/adult for each dichlorobenzene, based on the most conservative ADI provided by the WHO.

## ALPHA-HEXACHLOROCYCLOHEXANE (ALPHA-BHC; ALPHA-BENZENE HEXACHLORIDE)

Alpha-BHC is one of the most pervasive contaminants in the Great Lakes. The 1983 listing reports the compound in numerous locations. In fish, concentrations up to 0.06 mg/kg have been reported and one location in Lake Superior has reported levels in fish of 0.20 mg/kg. A mean concentration in water of up 0.015 ug/L was observed in 1978-79 in Lake Superior near Duluth, (I.J.C., 1983a).

Concentrations of alpha-BHC in fish and water are at a level of concern for human health. The Committee recommends further monitoring and evaluation. The Committee recommends an interim maximum daily exposure limit of 0.06 ug/adult, based on the U.S. EPA risk assessment data.

### Chlorinated Naphthalenes

1-CHLORONAPHTHALENE
2-CHLORONAPHTHALENE

Chlorinated naphthalenes were detected in Niagara River sediments, however, the concentrations in water were not given (I.J.C., 1983a). Neither Appendix E (I.J.C., 1978a) nor the 1983 Inventory provide data on concentrations in water or fish. The 1983 Inventory lists dichloronaphthalene in Lake Ontario.

There are no data to indicate whether or not chloronaphthalenes are at a level of concern for human health. However, the Committee recommends surveillance for chlorinated naphthalenes in surface waters. Toxicology research may be required, depending on the results of the surveillance. The Committee recommends an interim daily limit for all chlorinated naphthalenes of 3.2 ug/adult, based on the risk assessment for PCB.

### POLYBROMINATED BIPHENYLS (PBBs)

PBBs have been reported by the State of Michigan in carp from the Pine and Chippewa Rivers at 1.33 and 0.23 mg/kg fish, respectively. The 1983 Inventory lists PBBs in fish from northern Lake Michigan and the Pickerel River but does not give concentrations. PBBs have not been reported in water and are likely to exist only at exceedingly low concentrations.

Concentrations of PBB reported by the State of Michigan in carp from two rivers are at a level of concern for human health. Continued evaluation of fish monitoring data is recommended. The Committee recommends an interim maximum daily exposure limit of 0.04 ug/adult based on the Michigan risk assessment.

## POLYCHLORINATED TERPHENYLS (PCTs) (TCTs)

Polychlorinated terphenyls were detected in discharges to the Detroit River but Appendix E (I.J.C., 1978a) gives no details. According to the 1983 Inventory, tetra- and pentachloroterphenyls were detected in the Fox River, a tributary to Lake Michigan, but were not quantified. PCTs have not been reported in fish.

There are no data to indicate whether or not PCTs are at a level of concern for human health. Hence, the Committee recommends additional monitoring for PCTs to determine if they are present in the environment, especially in fish. The Committee has applied an uncertainty factor of 5000 (Weil, 1972) and recommends an interim maximum daily exposure limit of 0.5 mg/adult.

## Aromatic Hydrocarbons

### ETHYLBENZENE

Ethylbenzene was detected in the Niagara river at concentrations up to 0.2 ug/L (I.J.C., 1983a). The compound is widely used in chemical manufacturing, but is biodegradable in water. It was not reported in fish, however, and is not likely to be detected.

At present, reported concentrations of ethylbenzene in the Niagara River are not at a level of concern for human health. Monitoring is not recommended for fish or water.

### STYRENE

The database for this common industrial chemical shows one set of measurements only: concentrations in the Niagara River were between 1 and 10 ug/L (I.J.C., 1983a). Styrene was detected earlier in the Cleveland, Ohio water supply but was not quantified (I.J.C., 1978a). Levels in fish have not been reported.

Concentrations reported in water in the two inventories are not at a level of concern for human health. However, monitoring in fish is recommended until it is established that the levels are below the interim exposure limit.

## POLYCYCLIC (POLYNUCLEAR) AROMATIC HYDROCARBONS

BENZO(A)PYRENE
CHRYSENE
DIBENZ(A,H)ANTHRACENE
BENZO(B)FLUORANTHENE
BENZO(J)FLUORANTHENE

Chrysene has been found in sediments together with BaP. No data on contamination of fish are given in the two summaries.

Dibenz(a,h)anthracene has been found in the sediments of tributaries to Lakes Superior and Erie and in a discharge to the Detroit River. Concentrations in water are not known.

Benzo(b)fluoranthene is listed in both Appendix E (I.J.C., 1978a) and the 1983 Inventory as an air pollutant in the Detroit-Lake Huron-Sudbury region with concentrations of up to 1 $ug/m^3$. No data are given for its occurrence in water or fish.

Benzo(j)fluoranthene was detected in the waters of western Lake Erie but was not quantified (I.J.C., 1978a).

Reported concentrations of BaP in fish are not likely to be at a level of concern for human health, considering the amounts of PAH in other dietary sources. Exposure to PAH in developed areas like the Great Lakes basin is inevitable because of their widespread generation via combustion. However, there remains an inadequate data base for assessment of the other PAH.

## Phenols

### CRESOL, O-, M-, P-

The cresols are shown in the Appendix E (I.J.C., 1978a) as being discharged into Lake Michigan. No details are given. No data for these compounds are shown in the 1983 Inventory. Cresols are biodegradable, but the rates of breakdown vary.

The use of large quantities of cresols within the basin warrants efforts to detect these chemicals in the Great Lakes basin. Based on identification and quantitation, toxicological data may be required. The Committee cannot recommend an interim maximum daily exposure limit at this time.

### 2,4,6-TRICHLOROPHENOL
### 2,4,5-TRICHLOROPHENOL

Trichlorophenols are frequently contaminated with chlorinated dibenzo-p-dioxins and dibenzofurans. They are also likely metabolites and degradation products of a variety of chlorinated aromatic hydorcarbons and may be produced when water is chlorinated in the presence of phenol. They were reported in fish from the Niagara River in concentrations of up to 22 mg/kg (2,4,5-TCP) and 33 mg/kg (2,4,6-TCP) and in Niagara River water at concentrations up to 1 up/L each (I.J.C., 1983a). Appendix E (I.J.C., 1978a) also mentions 2,4,5-Trichlorophenol in Lake Michigan but gives no details.

Concentrations of both TCP isomers reported in fish from the Niagara River are at a level of concern for human health and monitoring is required. Levels in water are not at a level of concern. The Committee recommends an interim maximum daily exposure limit of 35 ug/adult for total trichlorophenols, based on the U.S. EPA risk assessment.

## Ethers

### 1,4-DIOXANE

This solvent was observed in several discharges into Lake Michigan near Chicago in concentrations of 1 ug/L (I.J.C., 1978a). Ambient water concentrations were not given. The 1983 Inventory does not list this compound.

Concentrations of 1,4-Dioxane in discharges near Chicago are at a level of concern for human health. However, little is known of the concentrations of dioxane in surface water or fish. Hence, the Committee recommends that data on the uses of dioxane be collected and that surveillance take place for this compound in effluents, surface waters near effluents and fish in the vicinity of effluents.

## Acids and Esters

### PHTHALIC ACID, DIISOBUTYL ESTER (DIISOBUTYLPHTHALATE, DBP)

This phthalic acid ester was reported in a wastewater discharge into Lake Michigan near Chicago (I.J.C., 1978a) at a concentration of 14 ug/L. The 1983 Inventory does not list this compound. The compound is probably more abundant than available data suggest.

The single wastewater discharge reported is not at a level of concern for human health. On the basis of the NAS evaluation, the Committee recommends an interim maximum daily exposure limit of 7.7 mg/adult.

### PHTHALIC ACID, BIS(2-ETHYLHEXYL) ESTER · BIS (2-ETHYLHEXYL) PHTHALATE, (DIETHYLHEXYL PHTHALATE, DEHP)

This compound is another pervasive contaminant in the Great Lakes basin ecosystem. It is found in fish at mean concentrations (for any series of specimens taken from any any site) of up to 1.3 mg/kg (Lake Superior), (I.J.C., 1978a and I.J.C., 1983a). The highest concentrations in ambient water were 137 ug/L (Lake Michigan), (I.J.C., 1978a), and 71 ug/L (Niagara River) (I.J.C., 1983a). A mean concentration of 47 ug/L was found in Wine Creek, a small tributary draining the PAS chemical waste site near Oswego, N.Y. (I.J.C., 1983a).

Based on new information on this compound, concentrations of DEHP in fish and water in several areas of the Great Lakes are at a level of concern for human health. The jurisdictions should examine, with appropriate monitoring, this issue and consider lowering the environmental concentrations of DEHP by placing restrictions on its use or by other appropriate means.

## Miscellaneous

### ANILINE

Aniline is not listed in the 1983 Inventory as a contaminant of Great Lakes biota, sediment, water or effluent. However, it was detected before 1978 in Muskegon, Michigan wastewater treatment plant influent, but not in the effluent, and was not quantified. These limited findings do not warrant an evaluation of the contamination with aniline at this time. Aniline is biodegradable in surface waters. Nevertheless, this chemical is used extensively by the chemical industry and therefore may appear as the result of accidental release.

Under these circumstances the Committee is not concerned with ambient concentrations of aniline but recommends that industrial discharges be examined for the presence of aniline.

### AZOBENZENE

Azobenzene is not listed in the 1983 Inventory as a contaminant of Great Lakes biota, sediment, water or effluent. However, it was detected before 1978 in Muskegon, Michigan wastewater treatment plant influent, but not in the effluent, and was not quantified. The Committee has no data on its present industrial use.

There are no data to indicate whether or not concentrations of azobenzene exist at a level of concern for human health.

However, the Committee recommends that the jurisdictions determine whether or not it is being used in the Great Lakes basin, and if so, that monitoring be implemented.

### 3,3'-DICHLOROBENZIDINE

3,3'-Dichlorobenzidine was found in discharges into Lake Michigan but was not quantified (I.J.C., 1978a).

While there are no data available to indicate whether or not this chemical is at a level of concern for human health, it has been reported in the basin. The Committee recommends that discharges of 3,3'-Dichlorobenzidine be quantified immediately to assess its potential health impact.

### NICKEL, AS METALLIC ION

Levels of nickel in fish and water of the Great Lakes are largely unknown.

There are no data to indicate whether or not concentrations of nickel are at a level of concern for human health. The Committee considers it unlikely that nickel occurs in concentrations that are of concern to human health in Great Lakes fish and water and does not recommend further monitoring.

## OTHER CARCINOGENS

The increased incidence of tumours in fish strongly suggests the presence of either carcinogens or promoters of carcinogenesis in the waters inhabited by these organisms. It is reasonable to assume that the occurrence of tumours indicates the presence of bioactive concentrations of such chemicals in the flesh of the affected fish. The extrapolation of significant tumour incidence in fish to mammalian populations is fraught with difficulties due to the uncertainties in the dose and latency relationships between fish and mammals. If these relationships were established, the response of fish to mixtures of carcinogens or to the presence of both carcinogens and promoters in water would be of interest and possibly would provide new and significant information for the assessment of the threat of cancer to humans.

The direct transmission of cancer to humans by the ingestion of fish cancerous cells or tumour viruses is almost certainly a misplaced conception.

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